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Illinois Institute of Technology

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Abstract

A composite solid, prepared by precipitating an Fe oxide onto granular activated carbon (GAC), was evaluated as an adsorbent for Cu(II) and Cı(VI) in aqueous solutions Relative to adsorption onto uncoated GAC, increasing Fe oxide coatings decreased adsorption capacities for Cr(VI) In contrast, Cu(II) adsorption capacity increased as the amount of Fe oxide increased, from about 1 4 mg/g for GAC to 5 mg/g for GAC coated with 37 mg Fe oxide/g GAC Tests in a column process for Cu(II) removal demonstrated that the composite adsorbent could be reused through at least 15 adsorption and desorption cycles Although a fraction of the adsorbed Cu(II) was retained by the solid, there was no apparent loss in adsorption capacity Treatment of low concentration solutions was effective, a 100 μg Cu(II)/L solution was reduced to no more than 3 μg/L through 1000 bed volumes processed Removal of complexed metals depends on the characteristics of the complex However, even when all the Cu(II) was complexed by EDTA, breakthrough was retaıded, pıobably by adsorption onto exposed GAC

Recovery and Recycle of Metals from Industrial Waste Water by Adsorption onto Fe Oxide-Coated Carbon

This document is the final report from the first phase of a project to evaluate Fe oxide-coated granular activated carbon (GAC) as an adsorbent for the removal and recovery of metals from water Background information summarizing related previous work and explaining the rationale behind this research is presented in Chapter 1 Following the introduction is a chapter on methodology, where the materials and techniques used in the experiments are described Chapter 3 presents results from the experiments, including characteristics of the composite Fe oxide-GAC adsorbent determined from batch and column adsorption tests A discussion of the results and conclusions from this study follow immediately in Chapters 4 and 5, respectively This report concludes with recommendations for future work (Chapter 6), including evaluation of how Fe oxide synthesis influences the adsorbent characteristics, assessment of how properties of the GAC such as surface area and pore volume distribution affect adsorption, and investigation of cocontaminant behavior

1 0 Introduction

A typical treatment process for waste waters in the metal finishing and electroplating industries involves some form of a precipitation process There are several potential disadvantages to these traditional techniques For example, prior treatment may be required to remove complexing agents that may inhibit precipitation (Bhattacharyya and Cheng, 1987) When precipitation does occur, the minimum solubility of the various metals in a mixed waste stream generally occurs at different pH values As a result, maximum removal of one metal may occur at a pH value where the solubility of another is unacceptably high Furthermore, given the increasingly stringent treatment and disposal regulations, a successful precipitation process may not be the optimal solution to waste water treatment problems The options for sludge management are becoming limited, the associated disposal costs are increasing, and the long-term liabilities associated with sludge disposal represent an ill-defined, growing concern for metal finishers and electroplaters To overcome these problems, metal finishing and electroplating industries need to evaluate recovery and recycle technologies

One potential recovery and recycle treatment technique involves the removal of metals by adsorption onto oxide adsorbents Adsorption processes have long been recognized as playing an important role in the retention of metals by soils (Jenne, 1968) and potential applications to industrial treatment have been discussed by Benjamin et al (1982) Adsorption processes have the potential to overcome many of the limitations associated with precipitation-based treatment techniques For example, the presence of complexing agents does not necessarily interfere with (Benjamin and Leckie, 1982) and, in some cases, may actually enhance metal adsorption (Davis and Leckie, 1978) Furthermore, although the soluble metal concentration in a precipitation process is fixed by the solubility of the metal, the soluble metal concentration in an adsorption process depends on the adsorbate-adsorbent ratio Increasing the adsorbent concentration will increase uptake, and removal to trace levels is possible Finally, because removal is pH-dependent, adsorption could be reversible Therefore, in waste water treatment adsorption could be used to not only remove metals but also recover and recycle them back into an industrial process

Among the more promising adsorbents for industrial waste treatment applications are the Fe oxides The feasibility of using Fe oxides to remove trace elements from waste water has been demonstrated and adsorption process parameters are discussed by Benjamin et al (1982) and in references cited therein More recently, Schultz et al (1987) examined adsorption and desorption of several metals (Cd, Cr(III), Cu, Ni, and Zn) with a freshly precipitated hydrous ferric oxide (ferrihydrite)

Their adsorption results were in agreement with previous studies, adsorption of cationic metals increased with increasing pH and reached nearly complete removal

The term Fe oxide is frequently used to represent a whole family of oxide, hydroxide, and oxyhydroxide Fe minerals Although these minerals have a variety of physical and chemical properties, one characteristic common to all of them is their small particle size When present as a discrete mineral phase, the particles are typically in the colloidal size range and difficult to remove from aqueous solutions Flotation or coagulation and sedimentation are feasible separation processes, but they typically require additional chemical treatment to destabilize the particles These added chemicals would increase the cost of the overall treatment scheme and, more importantly, complicate recovery and recycling of the metals An alternative approach is described by Edwards and Benjamin (1989) who prepared an Fe oxide-coated sand for use in an adsorption-filtration process The sand provided an inert support substrate and the added Fe oxide coating served to adsorb dissolved metals and enhanced the removal of particulate metals

The purpose of this research project was to investigate the performance of an Fe oxide-coated carbon to treat metal-bearing waste waters Relative to the Fe oxide-coated sand studied by Edwards and Benjamin (1989), Fe oxide-coated carbon has several potential advantages These include much higher specific surface areas and the absence of dissolved silica that can interfere in the adsorption of anionic metal-ligand complexes Previous studies have explored activated carbon by itself as an adsorbent for heavy metals, and observed that it was most effective in the presence of complexing agents (Bhattacharyya and Cheng, 1987, Ku and Peters, 1987) Activated carbon that is partially or fully coated with Fe oxide could be an effective adsorbent for both free and complexed metals

This adsorption process is conceptually similar to ion exchange processes, which have been successfully applied to waste water treatment in the electroplating industry (Peters and Ku, 1985, Mehta, 1989) Relative to traditional treatment process, both adsorption and ion exchange have several advantages There is the potential to recover and reuse metals with little or no sludge to dispose of, the processes are ideally suited for treating dilute concentrations, and the space requirements are minimal In addition, both processes are versatile in the sense that they can treat fluctuating flowrates and concentrations and be readily adapted to meet increasingly stringent effluent regulations Both processes also differ from traditional treatment in that they require more attention in terms of maintenance and monitoring, and there is a need to properly manage the regenerant Relative to ion exchange, the adsorption process has possible advantages in these last two areas For example, the same adsorbent would be used for metals that occur as cations or anions, only the solution pH would be changed to effect removal There are potential cost savings here because anionic resins are typically twice as expensive as cationic resins Furthermore, unlike organic ion exchange resins, Fe-coated carbon is relatively inert and less likely to be damaged by extreme temperatures or oxidants Finally, regeneration may be more efficient with an Fe oxide adsorbent Whereas a large excess of regenerant is typical for strong-acid resins, the desorption step with Fe oxide adsorbents is close to stoichiometric requirements Materials and experimental techniques designed to evaluate these advantages and other properties of the composite adsorbent are described in the next chapter

2 0 Methodology

This section begins with a description of the methodology and the kinds of analyses used It includes the GAC cleaning procedure and the synthesis procedures used to prepare the iron oxide solid and iron oxide-coated GAC Composite adsorbents were characterized by assessing several bulk and surface characteristics and, when appropriate, these properties were compared to similar properties of the end-member adsorbents, Fe oxide and GAC Reagent grade chemicals were used throughout this study unless specified, and all the labware was detergent and acid washed and rinsed with deionized water Analyses of iron, copper, or chromium followed standard atomic absorption spectrophotometry (AAS) techniques as described by Clesceri et al (1989)

2 1 Adsorbent Preparation

Granular activated carbon (GAC) used in this experiment was Calgon Carbon Corporation type TOG, provided courtesy of the manufacturer According to the product brochure, this GAC has a total N_2 BET surface area of 800-900 m^2/g, an apparent bulk density of 0 54 g/cm^3, a particle density of 0 78 g/cm^3, and a pore volume fraction of 0 82 Prior to use in this study the GAC was sieved between 425-600 μm, baked in an oven at 200°C for 2 d, and washed several times with deionized water by tumbling it in a roller for a day This GAC slurry was filtered, completely dried in an oven at 110°C, cooled in a desiccator, and stored at room temperature in a covered glass container until further use

Iron oxide-coated GAC (FeGAC) was prepared by mixing GAC with a known amount of $Fe(NO_3)_3$ solid and adding enough deionized water to cover the solid This suspension was mixed by shaking the container and then allowed to sit for a few hours so air trapped in the pores could escape Next, the mixture was dried in an oven at 90°C, cooled to room temperature, and washed several times with deionized water to remove detachable and discrete Fe oxide The resulting FeGAC composite adsorbent was dried in the oven at 105°C and stored at room temperature in a covered glass container until needed For comparison purposes, a reference Fe oxide was prepared following the same procedures except the GAC was omitted

2 2 Solids Characteristics

All solids were subjected to x-ray diffraction analysis, scanning electron microscopy (SEM), N_2 BET surface area measurements, and acid extractions to determine their Fe content In addition, the durability of the Fe oxide coating of the FeGAC composite adsorbents was evaluated in an abrasion test

For the x-ray analyses a sample of Fe oxide was spread on a glass slide smeared with petroleum jelly Other adsorbents were mixed with petroleum jelly and placed in an acrylic sample holder There was no interference in the diffraction spectrograph from the use of petroleum jelly BET surface area measurements were made with N_2 gas at the Institute of Gas Technology following standard procedures Extractable iron was estimated by boiling solids in concentrated HNO_3, and analyzing the extract by AAS

A durability test for the composite (FeGAC) adsorbents was performed by equilibrating a known amount of the solid (2 g/L) in a 0 01 M $NaNO_3$ solution at pH values of either 3, 7, or 11 in a mixed reactor for 24 h When necessary, acid or base was added to maintain the desired pH value The resultant solution was filtered through 0 45 μm filter paper and the filtrate was acidified, concentrated to a small volume, and analyzed for total iron using AAS

2 3 Adsorption Characteristics

Batch tests with model cation and anion adsorbates (Cu(II) and Cr(VI), respectively) were used to examine kinetics, capacity, and pH dependence Column tests were used only with Cu(II) to simulate a treatment process and compare this adsorbent to an ion exchange resin All tests were conducted in a 0 01 M $NaNO_3$ background electrolyte, and adsorbates were added from $Cu(NO_3)_2$ or $K_2Cr_2O_7$ stock solutions Samples were filtered (0 45 μm) and acidified prior to analysis by AAS

For batch adsorption experiments, the adsorbate copper concentration was 2 mg/L and the adsorbent concentration was 0 5 g/L These parameters were used so that the bulk solution would not become saturated with respect to copper hydroxide solid The contents of each container were mixed and the solution was maintained at pH 6 Sample aliquots were taken at 5 min intervals Desorption tests followed after a 2 h or 1 d adsorption time The desorption test was carried out by sequentially decreasing the pH of the solution from 6 to 3, approximately 20 min elapsed during each one unit pH change Samples taken from the above tests were filtered (0 45 μm) and the filtrate was acidified and analyzed for total Cu(II) by AAS The above procedure was repeated for Cr(VI) except the concentration was 10 mg/L and the solutions were equilibrated at pH 4 for adsorption and later desorbed at pH 10 Differences in pH for these batch experiments reflect the different adsorption behavior of cationic and anionic metals at oxide surfaces Cationic metals, such as Cu(II), exhibit increasing adsorption with increasing pH In contrast, anionic metal species, such as the chromate oxyanion, exhibit decreasing adsorption with increasing pH

In the capacity experiments, a separate solution of the Cu(II) adsorbate and a suspension of the composite adsorbent (0 1 g/L) were prepared in 0 01 M $NaNO_3$ solutions and adjusted to pH 6 Once the pH values had stabilized, the solution and suspension were combined so that the total Cu(II) concentration was 0 4, 0 8, 1 2, 1 6, or 2 0 mg Cu/L These suspensions were kept on a rotating rack for 2 h or 4 d After that period, solid and solution were separated by gravity settling or filtration and the samples analyzed In the capacity tests for Cr(VI) the concentrations used were 2, 4, 6, 8, or 10 mg Cr/L, the concentration of GAC or FeGAC adsorbents used was 0 5 g/L, and Fe oxide concentration was 0 05-0 1 g/L The tests were carried out at pH 4

Surface chemical characteristics of some of the solids were also evaluated using potentiometric titrations The technique involved titration of suspensions with acid or base in an indifferent electrolyte of constant ionic strength (0 01 M $NaNO_3$) under a nitrogen atmosphere When acid or base is added to a suspension of adsorbent particle, surface reactions take place Measurements of pH of these suspensions as a function of volume of acid or base added, can be used to describe the surface chemical characteristics of the solids, including the surface site density and the intrinsic surface hydrolysis constants Known amounts of solids were added to 500 mL volume plastic containers and deionized water was added until the volume of the suspension was 500 mL In each step of the titration it took about 6-8 h for the pH value to stabilize after aliquots of acid or base were added to suspensions of GAC or FeGAC adsorbents The equilibration time was comparatively very small (about 1-3 min) for Fe oxide solid The titration data were evaluated with FITEQL V 2 0 (Westall, 1982) to determine the surface hydrolysis reactions of the solid oxides

Test columns were made from 1 5" O D , 1 0" I D polymethylmethacrylate tubes In all column tests, 15 cm^3 of medium was placed in the column and the resulting bed depth was about 3 cm The flow rate was 5 cm^3/min and the theoretical hydraulic residence time was 1 min

In some of the column experiments, an ion exchange resin was used for comparison The resin was Amberlite IR-120 Plus, recommended and supplied, courtesy of the manufacturer, for Cu(II)

removal This resin has a styrene-divinyl-benzene matrix structure, an effective size of 0 50 mm, a moisture content of 45%, and a total exchange capacity of 1 9 meq/mL The ion exchange resin was converted to the Na form prior to use in the column tests by washing twice in deionized water, immersing it in 2 N Na_2SO_4 for 24 h, rinsing twice in deionized water, loading it into the column where it was air-dried, and storing in a covered glass container until needed

3 0 Results

Results from two types of analyses are presented in this section Whenever possible, adsorbents were evaluated in situ, as was the case in the various adsorption tests These types of tests can provide a description of the solids under operating conditions In contrast, for analyses such as the SEM, x-ray diffraction, and surface area determinations, it was necessary to dry the solid prior to the analysis Although this processing is a necessary part of the standard measurement technique, it is possible that the surface characteristics of the solid were altered by drying As a result, the surfaces "seen" by these analyses may be different from the surfaces "seen" by the in situ analyses Until more sophisticated analytical techniques become available, this caveat should be kept in mind Although the entire suite of analyses may be viewed as complementary, perhaps more weight should be given to the results of the in situ analyses

3 1 Solids Characteristics

The evaporative deposition process became less effective as the applied $Fe(NO_3)_3$ dosage was increased (Figure 1) For applied Fe dosages of 40, 80, and 120 mg Fe/g GAC, the observed coatings were 37, 52, and 72 mg Fe/g GAC, respectively

Figure 1 Fe oxide coating efficiency onto GAC

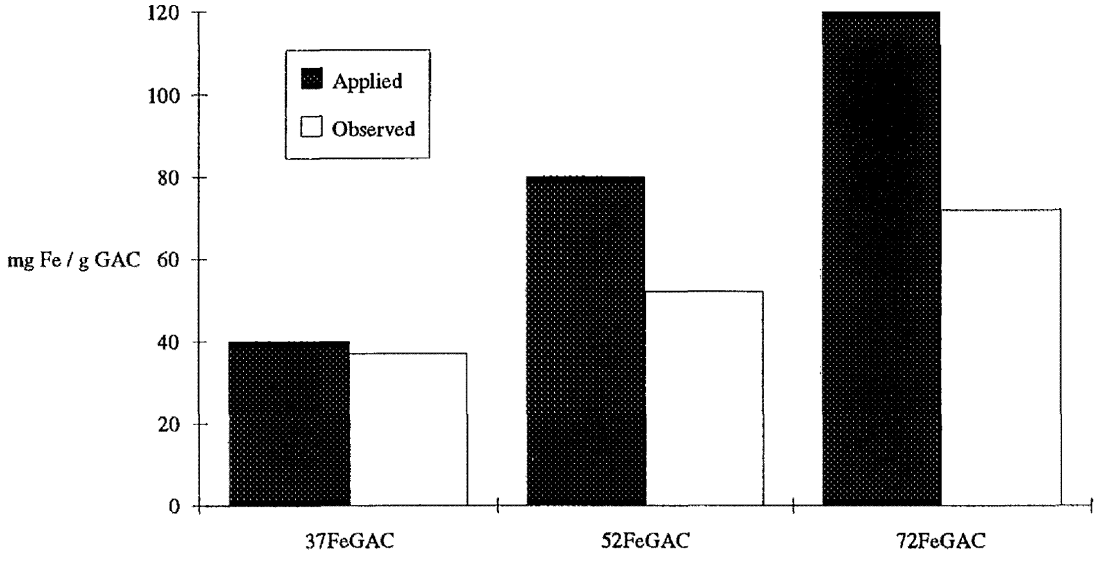
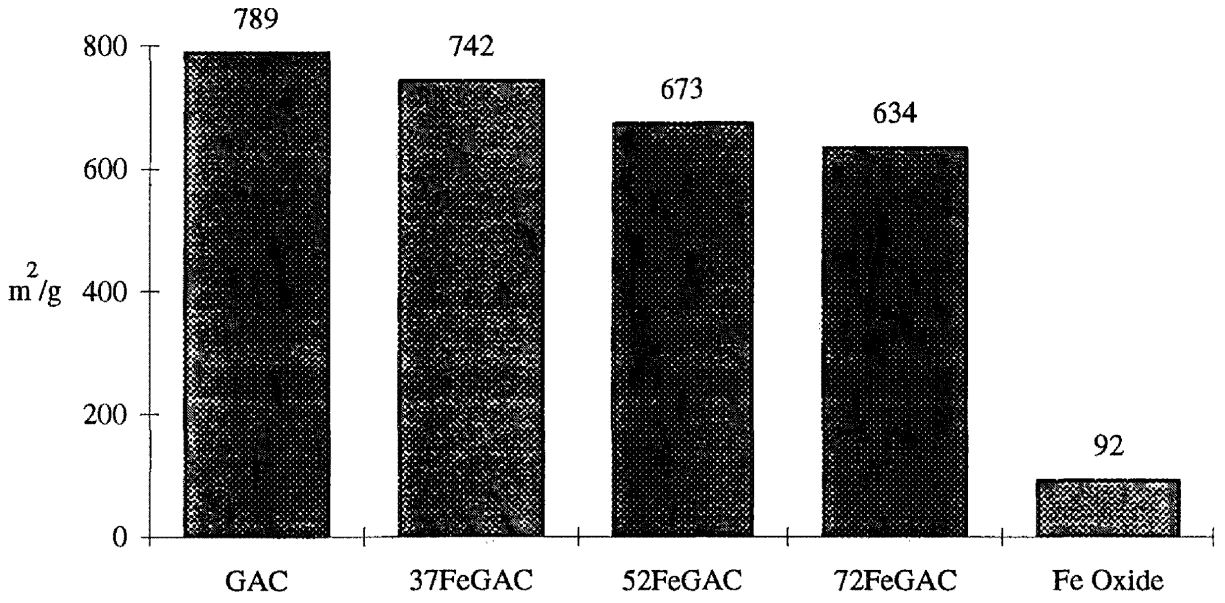


Figure 2 summarizes the results of the surface area measurements for GAC, Fe oxide, and the composite adsorbents Relative to the Fe oxide, the surface area of the GAC was nearly nine times greater The effect of depositing the low surface area Fe oxide onto the GAC is evident for the composite adsorbents, whose area decreased with increasing Fe oxide content

Figure 2 N_2-BET surface areas for the solids



Diffractograms from the x-ray analyses are presented as a composite figure so the adsorbents can be compared (Figure 3) Because the signal amplitude was not the same for all solids, however, only the relative peak heights for one solid and the peak locations (2Θ values) among the solids should be compared In contrast with the GAC, which was a relatively x-ray amorphous solid, the diffractogram for Fe oxide had distinct x-ray peaks, many of which were consistent with hematite In general, diffractograms for the composite solids suggest materials with x-ray characteristics somewhere between the GAC and Fe oxide end-members, broad peaks near 2Θ values of 44 and 25 degrees resemble GAC, and sharper peaks suggest a crystalline structure more like the Fe oxide Locations and relative heights of the distinct peaks do not match peak locations for other, common Fe oxides

3 2 Adsorption Kinetics

Relative adsorption kinetics for Cu(II) removal was compared for all of the solids (Figure 4) The reference end-member adsorbents exhibited the extremes of the adsorption behavior, with relatively rapid adsorption in the Fe oxide suspension and the slowest adsorption in the GAC suspension The composite adsorbents fell between these two extremes and Cu(II) adsorption capacity appeared to increase with increasing Fe oxide coating

Surprisingly, many results of batch adsorption experiments with $Cr_2O_7^{2-}$ were in contrast to the behavior of Cu(II) The Fe oxide adsorbent still had the fastest adsorption kinetics and greatest adsorption capacity (Figure 5) However, relative to the uncoated GAC, the adsorption capacity decreased as the amount of Fe oxide on the GAC increased

Figure 3 X-ray diffraction patterns for various adsorbents Common x-ray peaks are shown for goethite (1), hematite (2), and ferrihydrite (3)

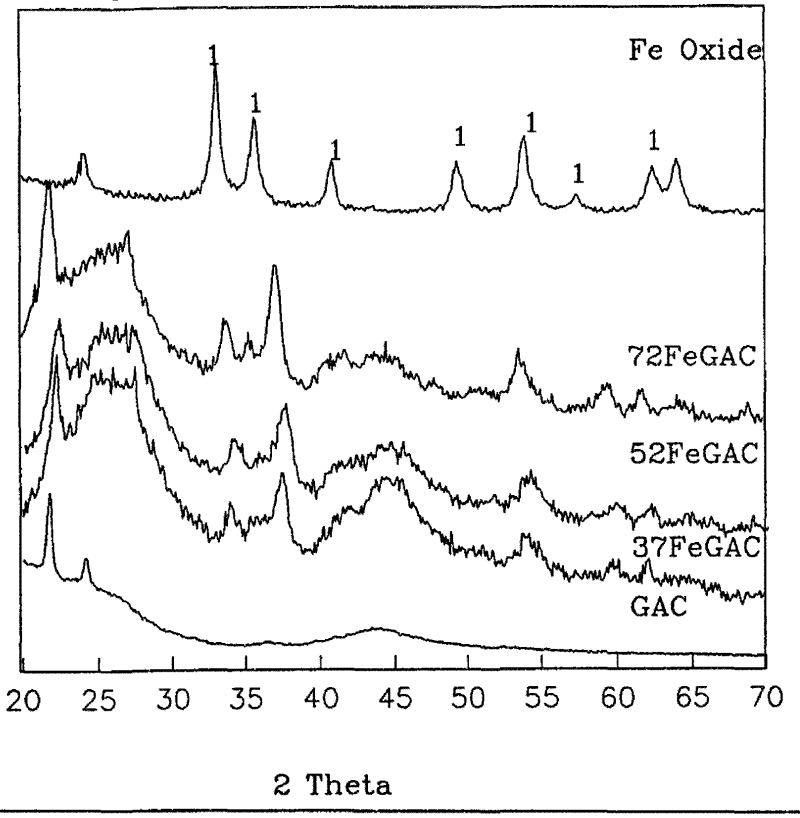


Figure 4 Rate of Cu(II) removal by various adsorbents Adsorbent concentration = 0 5 g/L and pH = 6

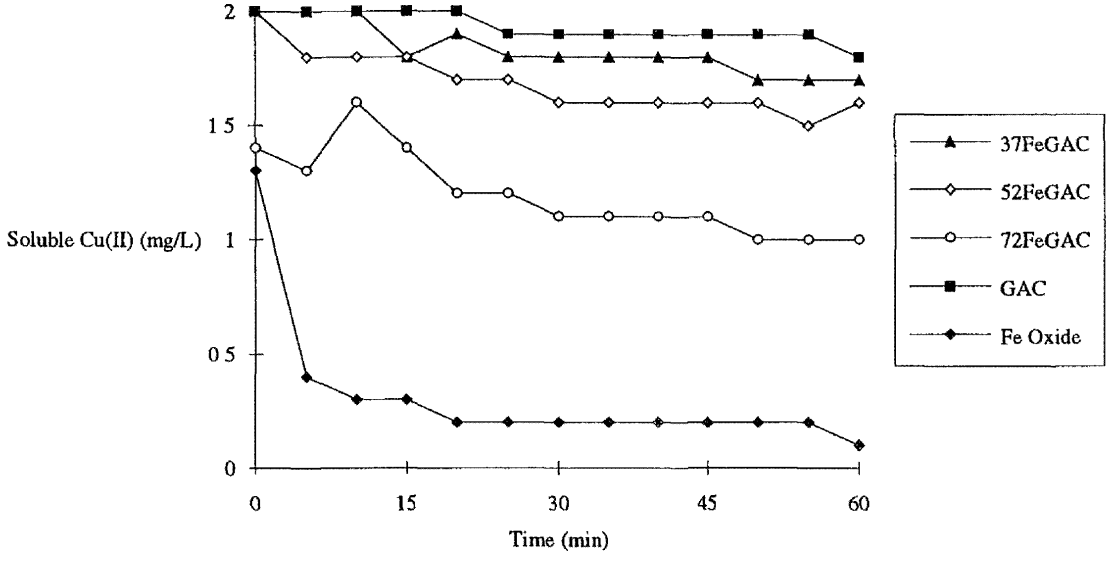
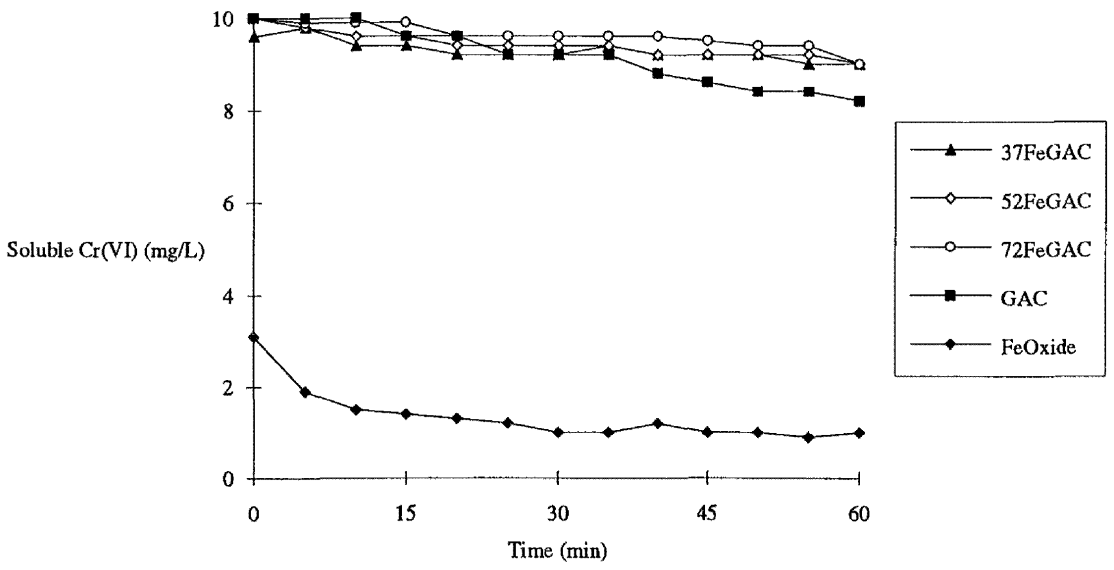


Figure 5 Rate of Cr(VI) removal by various adsorbents Adsorbent concentration = 0 5 g/L and pH = 4



3 3 Adsorption Capacity

Results from traditional isotherm experiments with these solids indicated that adsorption capacity varied among the solids and suggested that in some cases diffusion played an important role in the removal process After a 2 h contact time, the Cu(II) adsorption capacity was the least for GAC, slightly increased for the FeGAC composite adsorbents, and the greatest for the Fe oxide (Figure 6) Following a 96 h contact period the capacity of all adsorbents increased but this same sequence was observed (Figure 7) The relative increase in capacity, however, was considerably greater for the composite adsorbents than it was for either Fe oxide or GAC Freundlich isotherm parameters calculated from these data are summarized in Table 1

After 96 h, the amount of Cu adsorbed on the 52FeGAC and 72FeGAC composite adsorbents was about the same as the amount adsorbed on the Fe oxide Furthermore, because GAC by itself had a relatively small Cu(II) removal capacity, most of the removal by the composite adsorbents must have been due to the presence of the Fe oxide To explore this concept further, the adsorption isotherm data were normalized to the amount of Fe present (Figure 8) Interestingly, all three of the composite adsorbents appear to have the same adsorption capacity for Cu(II) In addition, relative to the discrete Fe oxide, this normalized capacity of the FeGAC adsorbents is at least three times greater

Adsorption isotherm experiments with Cr(VI) reinforce the behavior suggested by the kinetic study Isotherms calculated after 2 and 24 h contact times (Figures 9 and 10, respectively) indicate that in all cases, the presence of an Fe oxide deposit on the GAC reduces its adsorption capacity for Cr(VI)

Figure 6 Cu(II) adsorption isotherms for various adsorbents Solutions were in contact with the solid for 2 h at pH = 6 Solid lines in the figure are Freundlich isotherms (Table 1) Symbols are 37FeGAC (Δ), 52 FeGAC (✧), 72 FeGAC (○), GAC (■), and Fe Oxide (◆)

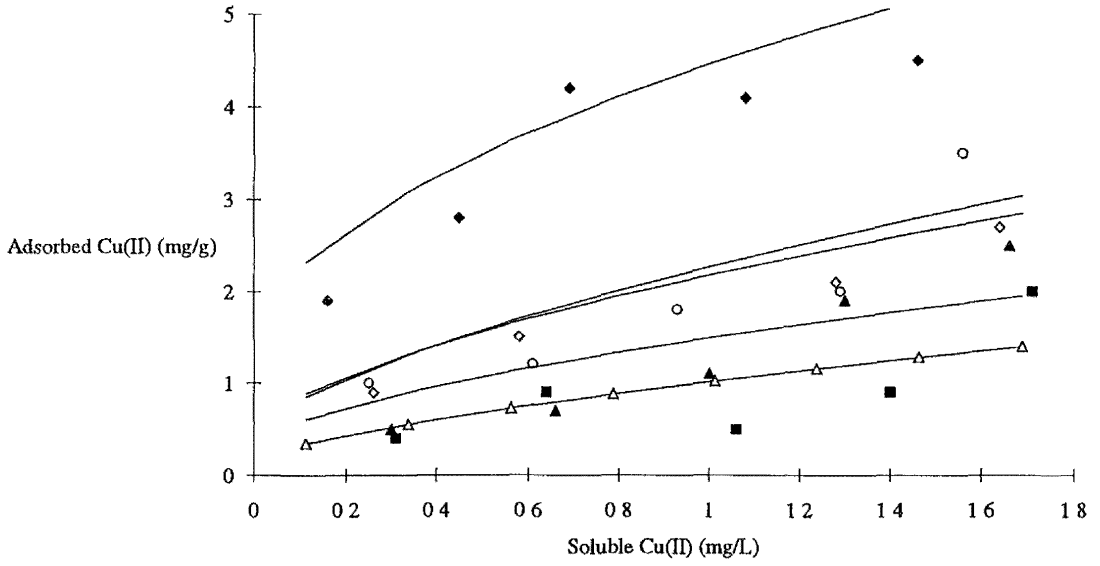


Figure 7 Cu(II) adsorption isotherms for various adsorbents Solutions were in contact with the solid for 96 h at pH = 6 Solid lines in the figure are Freundlich isotherms (Table 1) Symbols are 37FeGAC (Δ), 52 FeGAC (✧), 72 FeGAC (○), GAC (■), and Fe Oxide (◆)

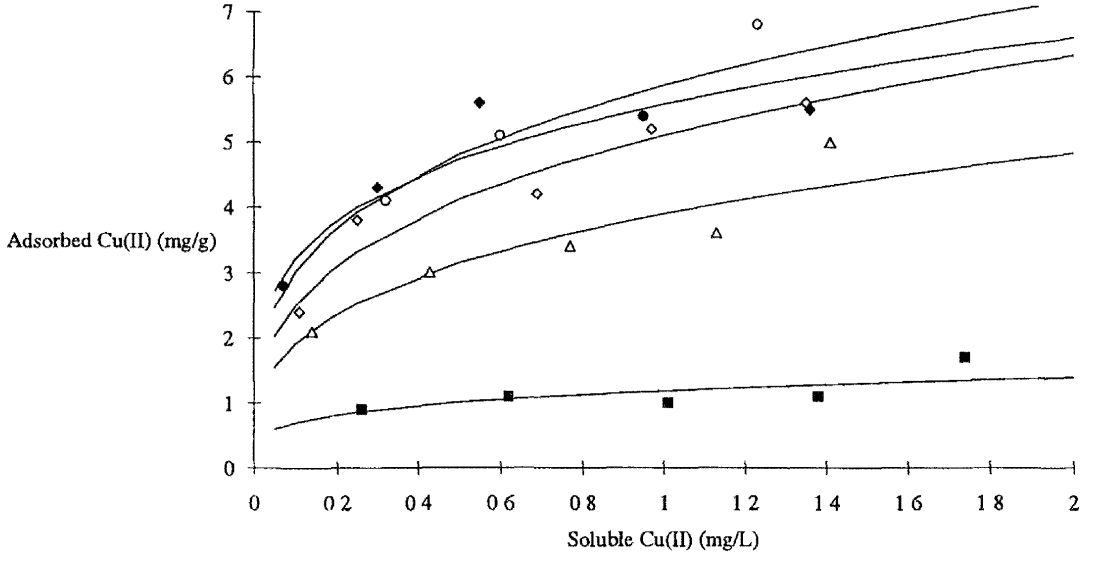


Table 1 Freundlich isotherm parameters for various adsorbents at both 2 h and 96 h contact times The model is (x/M) = a C^b, where (x/M) = mg/g, C = mg/L, a = $(L/g)^b$, and b is dimensionless Parameters were calculated from the data in Figures 6 and 7

adsorbent	2 h contact		96 h contact	
	a	b	a	b
GAC	0.88	0.67	1.19	0.23
37FeGAC	1.32	0.95	3.90	0.32
52FeGAC	1.93	0.56	5.10	0.31
72FeGAC	1.99	0.61	5.87	0.29
Fe oxide	4.09	0.41	5.58	0.24

Adsorption may not be the only removal mechanism in these systems Bowers and Huang (1987) reviewed activated carbon process for the treatment of Cr(VI)-containing waters and described two mechanisms for removal of Cr(VI) by GAC Adsorption was the dominant mechanism down to at least pH = 4, and possibly down to pH = 2 5 where they reported a maximum adsorption density of around 80 mg Cr(VI) per g GAC At pH values less than 2 5 they observed a rapid reduction of Cr(VI) to Cr(III) at the GAC surface Because our experiments were conducted at pH = 4, it is unlikely that Cr(VI) was reduced during these tests

Figure 8 Cu(II) adsorption isotherms normalized to Fe content Solutions were in contact with solid for 96 h at pH = 6

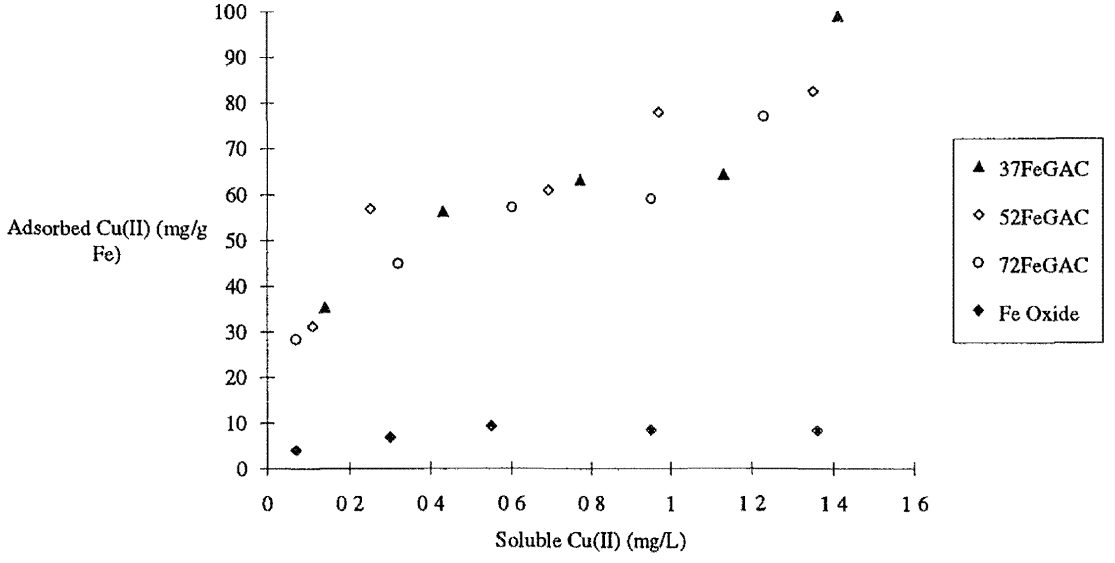


Figure 9 Cr(VI) adsorption isotherms for various adsorbents Solids were in contact with solution at pH = 4 for 2 h

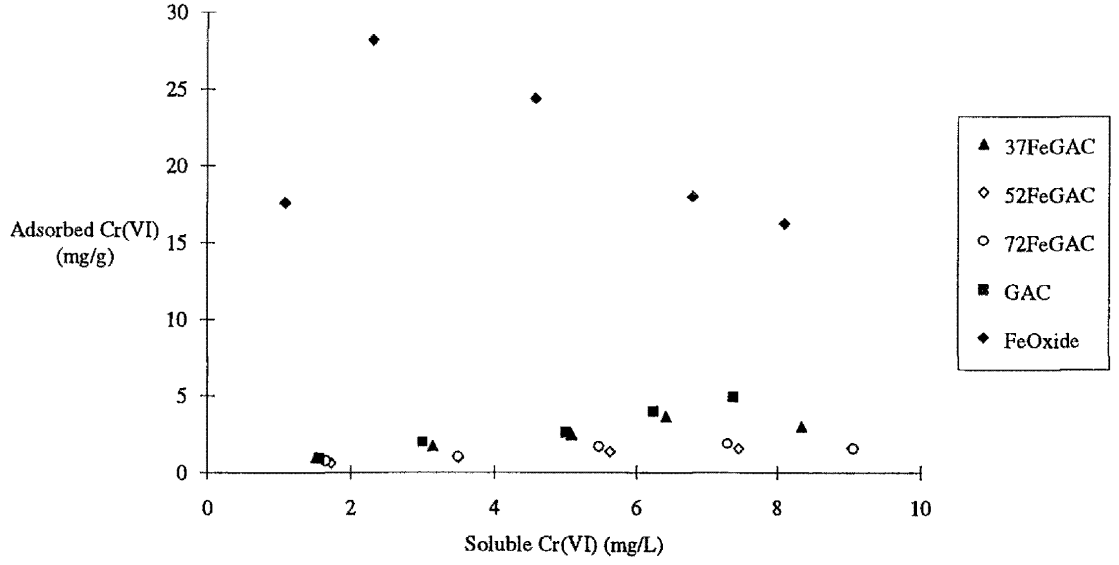
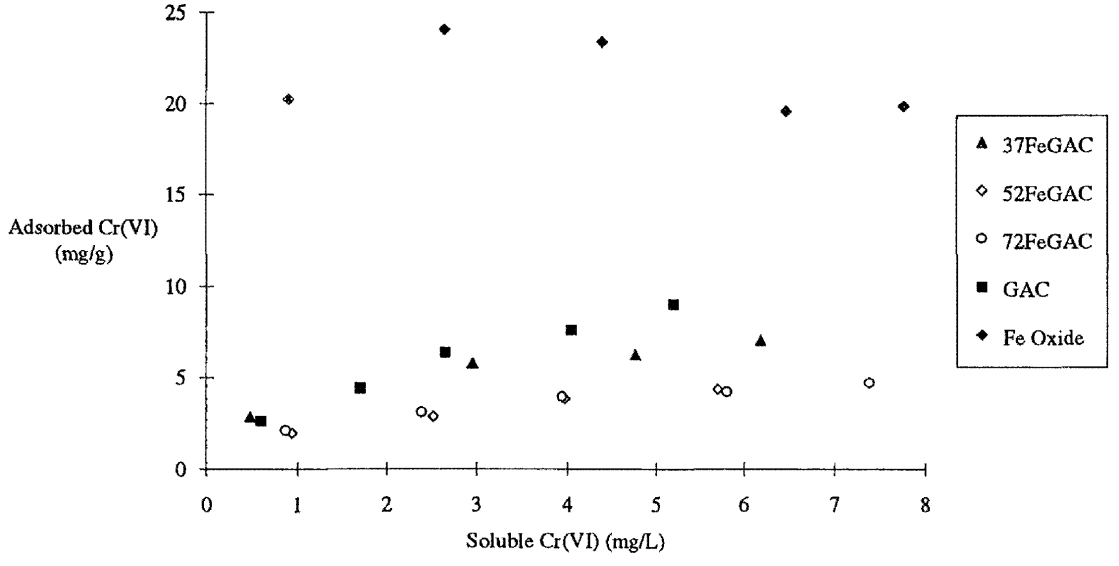


Figure 10 Cr(VI) adsorption isotherms for various adsorbents Solid was in contact with solution for 24 h at pH = 4



Because there were apparent inconsistencies between the adsorption behavior of Cu(II) and Cr(VI), the surface response to potentiometric titration was also examined Whereas the adsorption experiments probed the surface response to Cu(II) and Cr(VI), the titration tests probed the surface response to protons Data from the titration experiments for GAC, discrete Fe oxide, and 37FeGAC were evaluated using FITEQL V 2 0 (Westall, 1982) FITEQL uses a nonlinear, least-squares optimization technique to calculate equilibrium constants from chemical data The parameters calculated from the titration data were the surface binding site concentration and equilibrium constants for the following reactions

$$K_{+} = \frac{[SOH_2+]}{[SOH]\,[H^+]} \exp(-F\,\Psi / R\,T)$$

$$K_{-} = \frac{[SO^-]\,[H^+]}{[SOH]} \exp(-F\,\Psi / R\,T)$$

In these expressions SOH represents a surface hydroxyl group that can take on or give up a proton and the exponential term is a correction factor for the work of moving the proton through the electrical double layer This evaluation was based on the assumptions that hydroxyl groups were the dominant surface functional groups for each of the solids, and that surface complexation reactions could be described by the diffuse layer model More detailed descriptions of these types of surface reactions are available from Dzombak and Morel (1990)

Unfortunately, FITEQL would not converge for the Fe oxide titration data Initial input to the FITEQL model included the titration data, adsorbent concentration, and adsorbent specific surface area Among these parameters, the specific surface area is probably the most suspect because the N_2-BET analysis for surface area requires a dry solid It is possible that during the drying process the Fe oxide surface area could be decreased as a result of particle agglomeration or changes in the solid morphology To explore this possibility, FITEQL was used to reevaluate the titration data and surface area was used as a fitting parameter In these tests, the set of model parameters (log K_{+}, log K_{-}, site density, surface area) that provided the best fit to the model (lowest values of sum-of-squares/degrees of freedom) was selected as the best description of the surface (Table 2)

Table 2 Surface chemical characteristics for GAC, Fe oxide, and 37FeGAC

Parameter	GAC	37FeGAC	Fe Oxide
log $K_{+(int)}$	6 30	5.27	8.29
log $K_{-(int)}$	-7 69	-7 34	-10 60
binding sites (mol/g)	$2\,0\times10^{-4}$	$3\,1\times10^{-4}$	$2\,7\times10^{-4}$
pH_{ZPC}	7 0	6 3	9 5
Model surface area (m^2/g)	800	450	300
N_2 BET surface area (m^2/g)	789	742	92

Our results for GAC are consistent with the work of Corapcioglu and Huang (1987), who examined the surface chemical characteristics of 14 commercially available GAC's They observed surface areas ranging from 410 to 2162 m^2/g, and an average site concentration of 1 7×10^{-4} mol/g can be calculated from their data The pH_{ZPC} values calculated from their titration data ranged from 4 0 to 10 6

With the possible exception of the pH_{ZPC}, the surface characteristics for Fe oxide in Table 2 are also in the expected range Measured values of pH_{PZC} for Fe oxides are typically between pH 7 and 9 (Parks, 1964) Hesleitner et al (1987) synthesized hematite and also characterized the surface using titration data and the diffuse layer model They reported the following values $\log K_{+(int)} = 6\ 21$, $\log K_{-(int)} = -8\ 43$, binding site density = $1\ 3\times10^{-4}$ mol/g, $pH_{ZPC} = 7\ 2$, and a N_2-BET surface area of 13 2 m^2/g

Except for the surface area estimates, the composite adsorbent (37FeGAC) has surface chemical characteristics that are different fiom the mass-weighted sum of the two component parts Relative to the discrete GAC and Fe oxide solids, the concentration of surface binding sites for 37FeGAC is 1 5 and 1 1 times greater, respectively Surprisingly, the composite solid has a lower pH_{ZPC} value than do either of the components

A comparison of the surface area estimates in Table 2 is especially interesting, and our results suggest that FITEQL could be used to provide a meaningful in situ assessment of surface area For example, the FITEQL and N_2-BET surface area estimates for GAC are in excellent agreement This result seems reasonable for a rigid solid, such as GAC, whose structure should not change during the drying process In contrast, if the Fe oxide is not a stable solid, the higher surface area, hydrated form might shrink during the drying process, our results indicate a hydrated surface area three times larger than the dried surface area Finally, for the composite solid, a surface deposit of hydrated Fe oxide could block pores in the GAC, whereas if the Fe oxide shrinks during drying the surface area inside those pores would then be exposed Our results suggest that Fe oxide on the surface blocked over 50% of the GAC surface when the solid was in solution After drying, however, the surface Fe oxide blocked less than 10% of the GAC surface

Removal data were also generated from the column experiments In one series of tests, the capacity of GAC, 37FeGAC, and the ion exchange resin were compared (Figure 11) After 1200 bed volumes were processed, the GAC had nearly reached complete breakthrough, 37FeGAC was near 50% breakthrough, and the ion exchange resin was still achieving about 100% removal

To assess the capacity of the 37FeGAC, another test was conducted in an attempt to reach complete breakthrough However, after about 2000 bed volumes were processed, something changed in the removal process and the effluent Cu(II) concentration appeared to be in a steady state condition (Figure 12) It is possible that there was a solid state diffusive flux into the adsorbent, balanced by the flux of Cu(II) to the surface If so, what appears to be a slight upward trend after 8000 bed volumes should continue and the effluent concentration should return to the influent value Alternatively, the results may reflect a surface precipitation process in which a solid such as $Cu(OH)_2$ or $CuOHNO_3$ is precipitating at the surface (Farley et al , 1985) If so, then the effluent concentration should remain around 1 6 mg/L indefinitely

In summary, when an Fe oxide was deposited onto the GAC, the adsorption capacities of the solid for Cu(II) and Cr(VI) increased and decreased, respectively The adsorption capacity with respect to Cu(II) was assessed by three different techniques, site densities, adsorption isotherms, and column adsorption capacities

Figure 11 Cu(II) breakthrough curves for removal by three different media Column loading = 5 mL/min, bed volume = 15 mL, pH = 6, and influent Cu(II) = 2 mg/L

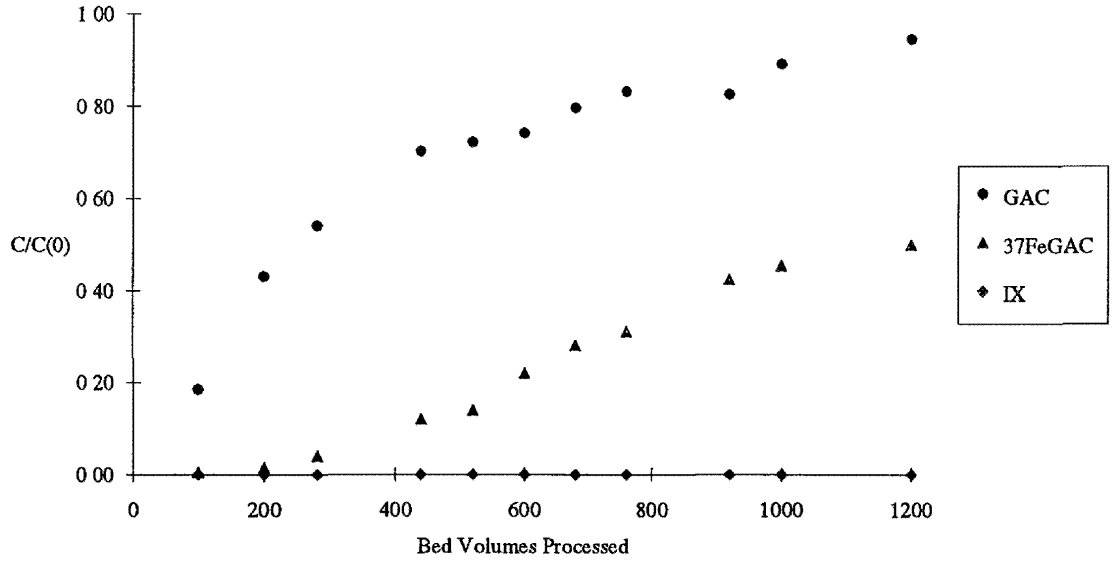
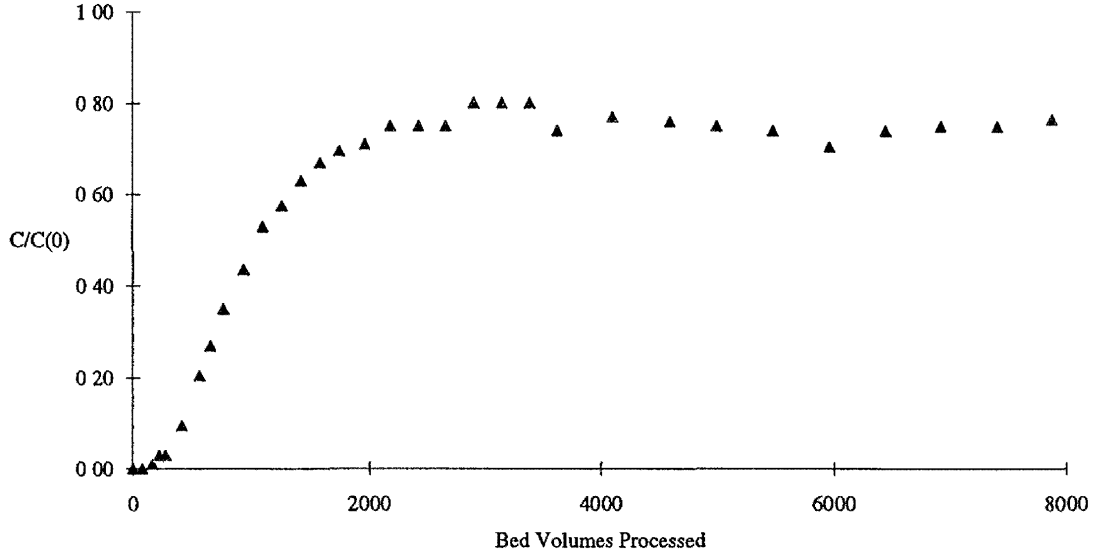


Figure 12 Breakthrough curve for Cu(II) removal by 37FeGAC Influent Cu(II) = 2 mg/L, loading = 5 mL/min, bed volume = 15 mL, and influent pH = 6



Total binding site densities estimated using data from titration experiments and the program FITEQL are reported in Table 2 Those values were 2.0×10^{-4} mol/g, 2.7×10^{-4} mol/g, and 3.1×10^{-4} mol/g for GAC, Fe oxide, and 37FeGAC, respectively In terms of surface reactions with protons, 37FeGAC has 1.5 and 1.1 times the number of sites of GAC and Fe oxide, respectively

Practical removal capacities for Cu(II) are probably more reliably estimated from the batch and column adsorption experiments Capacity estimates from the batch adsorption tests were obtained by using the isotherm parameters in Table 1 and extrapolating to calculate the surface loading in equilibrium with a concentration of 2 mg/L Capacity estimates from the column tests were obtained by integrating the area outlined by the breakthrough curves (Figures 11 and 12) Because 100% breakthrough was not observed for Cu(II) removal onto 37FeGAC (Figure 12) and because removal after 2000 bed volumes may be due to surface precipitation, the capacity estimate was based on total removal up to 2000 bed volumes Results from these capacity measurements are summarized in Table 3

The column and batch capacity estimates for Cu(II) removal by GAC are in good agreement Furthermore, because the 2 h and 96 h tests give identical results, adsorption kinetics does not appear to be a factor in batch tests with GAC (at least up to 96 h) In contrast, adsorption kinetics did play a role in Cu(II) removal onto 37FeGAC because the capacity increased 180% from 2 h to 96 h The fact that the 37FeGAC column test estimate is in better agreement with the 96 h batch study probably reflects the similar exposure time in these experiments Contact time for 2000 empty bed volumes during the column test was 100 h The good agreement between the 96 h batch study and the 37FeGAC column test also suggests that adsorption was the dominant removal mechanism in the column up to 2000 bed volumes Additional tests are required to determine if surface precipitation is an important factor when more bed volumes are processed

Table 3 Cu(II) removal capacity for GAC and FeGAC estimated from batch and column tests Estimates are based on a solution equilibrium concentration of 2 mg/L and pH = 6 except for the column test for 37FeGAC (see text)

Method	Cu(II) adsorption capacity (mg/g)	
	GAC	37FeGAC
Freundlich isotherm, 2 h contact	1.4	2.6
Freundlich isotherm, 96 h contact	1.4	4.9
Column breakthrough	1.3	5.0

Finally, based on the manufacturer's reported ideal capacity of 1.9 meq/mL for the ion exchange resin, we estimate an ideal capacity of 140 mg Cu(II)/g resin However, because the method of regeneration influences operation, the actual resin operating capacity will be somewhat lower Assuming a reasonable range from 0.9 to 1.4 meq/mL (Clifford, 1990), we estimate an operating capacity from 66 to 103 mg Cu(II)/g can be estimated Relative to the 37FeGAC, this ion exchange resin has from 13 to 21 times more capacity

Additional information about the Cu(II) removal process can be found by examining how the pH of the effluent changes as a function of the number of empty bed volumes processed (Figure 13) For example, the ion exchange resin, which was converted to the Na form prior to these tests, did not release protons during exchange, and the effluent pH remained similar to the influent pH throughout the process

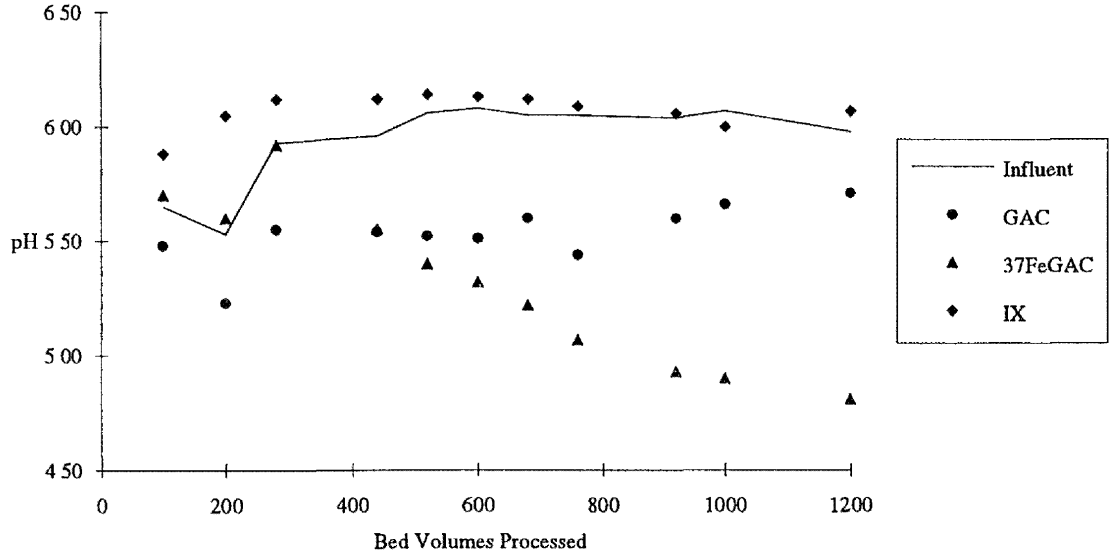
In contrast to the Na form ion exchange resin, protons should be released when Cu(II) adsorbs onto either GAC or FeGAC A simple description of the stoichiometry is

$$SOH + Cu^{2+} = SOCu^{+} + H^{+}$$

If no other processes affected pH, the effluent pH would initially drop to a steady state value reflecting the stoichiometry of the Cu(II) removal reaction As breakthrough occurred and the Cu(II) concentration in the effluent increased, the effluent pH would also increase as fewer protons were released within the column When the column reached saturation with respect to Cu(II) removal, proton release would stop, and the effluent pH would return to the same value as the influent An ion exchange resin operated in the H form would exhibit similar behavior

Protons released from the solid during adsorption, however, do not move passively through the GAC or FeGAC columns Instead, as demonstrated in the titration experiments, protons react with surface sites that are not fully protonated This reaction is equivalent to an acid titration of the medium downstream from the Cu(II) adsorption mass transfer zone (MTZ) In effect, there is a proton MTZ preceding the Cu(II) MTZ through the column As a result, the column has a pH buffering capacity that modifies the effluent pH curve If all the protons initially released react with surface sites, the effluent pH will remain the same as the influent pH When the proton MTZ begins to reach the end of the column, the effluent pH should fall to some minimum value and, as the Cu(II) MTZ reaches the end of the column, return to the pH value of the influent

Figure 13 Influent and effluent pH for Cu(II) removal by three different media Influent Cu(II) = 2 mg/L, loading = 5 mL/min, bed volume = 15 mL



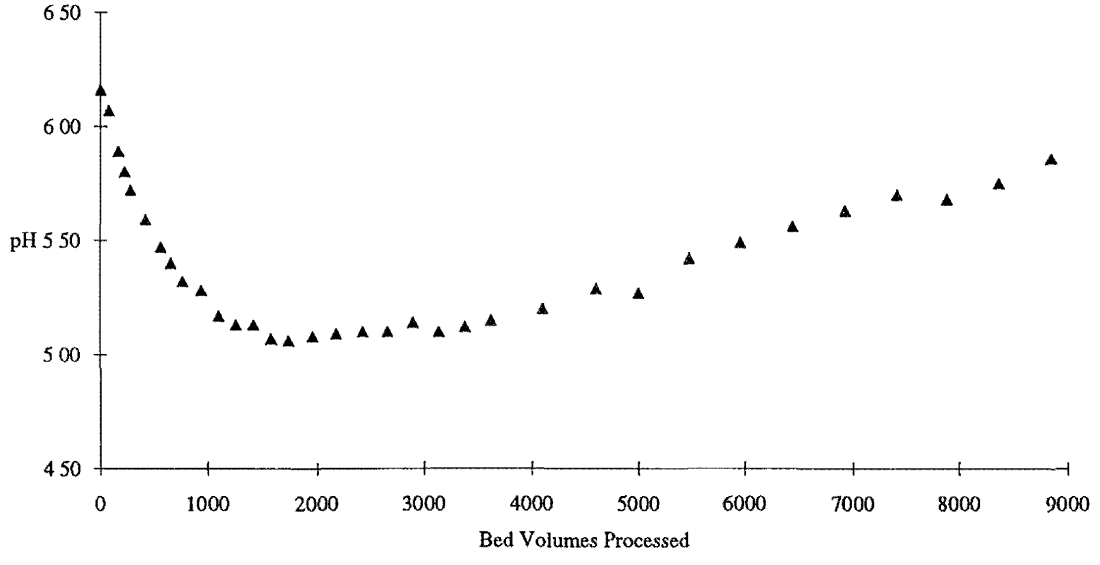
Surprisingly, the effluent pH curve for GAC indicates that proton release was nearly constant through the test (Figure 13), despite the fact that 100% Cu(II) breakthrough occurred after about 1200 bed volumes were processed (Figure 11) This observation suggests that even though Cu(II) was no longer being adsorbed, protons were still being released within the GAC The most likely explanation for this phenomenon is related to the difficulty in pre-equilibrating the GAC column to the desired pH = 6 Apparently there was excess acid in the GAC at the start of the test, which showed up as a continued slow release of protons

The effluent pH curve for FeGAC follows the expected pattern, initially decreasing to an apparent steady state value (Figure 13) and gradually increasing toward the influent pH value (Figure 14)

3 4 Regeneration and Recycle

Regeneration or desorption of adsorbed metals was investigated in batch experiments with both Cu(II) and Cr(VI), and in column experiments with Cu(II) In several of the column tests, the FeGAC medium was cycled through several adsorption/desorption processes to evaluate adsorbent recycle potential

Figure 14 Effluent pH for Cu(II) removal by 37 FeGAC Influent Cu(II) = 2 mg/L, loading = 5 mL/min, bed volume = 15 mL, influent pH = 6



Even though Cr(VI) adsorption onto several solids was minimal, desorption efficiency was examined In general, desorption was more efficient from solids with more Fe oxide content (Figure 15) However, when Fe oxide was present adsorption tended to be more sensitive to changes in the contact time, longer contact times prior to desorption decreased the amount of Cr(VI) recovered

Desorption efficiency was also examined in a series of experiments where Cu(II) was allowed to adsorb onto a solid for either 2 h or 24 h at pH 6, the solid was removed and transferred to another solution at pH 3, and the Cu(II) was allowed to desorb for about 20 min In contrast with the behavior observed for Cr(VI), when GAC was present adsorption tended to be more sensitive to changes in the contact time, longer contact times prior to desorption decreased the amount of Cu(II) recovered (Figure 16)

Because a longer adsorption contact time appeared to inhibit Cu(II) desorption and because the earlier results indicated that adsorption in column studies was similar to long-term batch tests, additional regeneration tests were conducted during the column tests In one series of tests, the adsorption step was terminated when the GAC column reached 100% breakthrough (after 1200 bed volumes, see Figure 11) and the column was regenerated in an attempt to recover adsorbed Cu(II) In general, desorption efficiency was inversely related to the adsorbent capacity (Figure 17) The fraction of adsorbed Cu(II) recovered ranged from a maximum of 40% for the GAC to negligible amounts for the ion exchange resin Desorption efficiency increased for GAC and FeGAC with decreasing pH of the regenerant solution The ion exchange resin, which is normally regenerated with concentrated sulfuric or nitric acid (pH < 1), did not release any Cu(II) under these conditions

Figure 15 Cr(VI) desorption from various solids at pH = 10 after either 2 or 24 h contact times at pH = 4

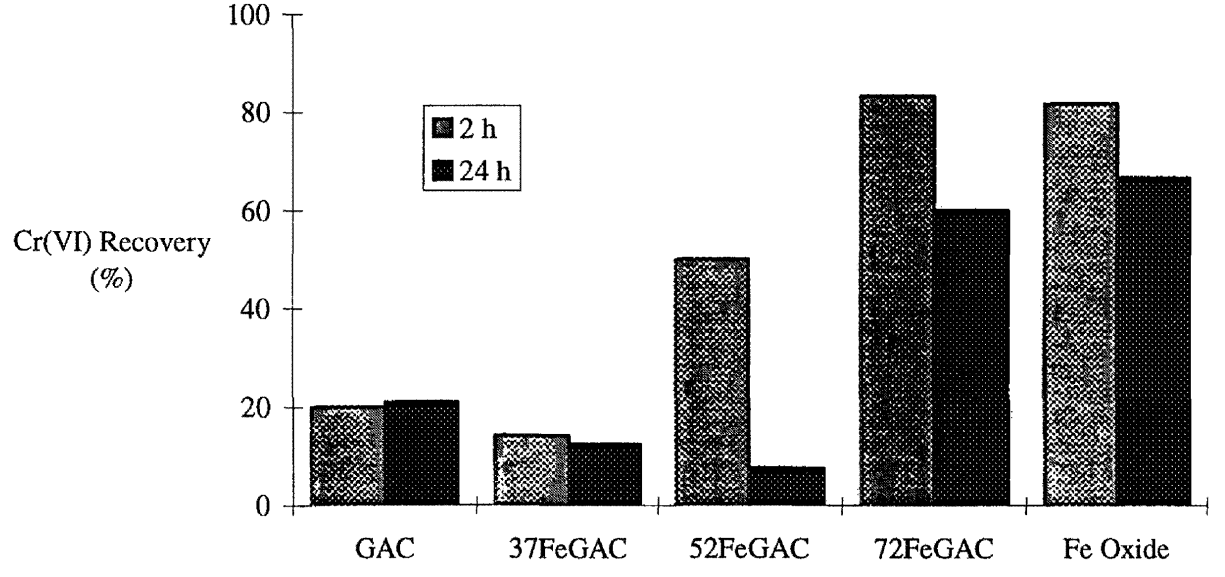


Figure 16 Cu(II) desorption from various solids at pH = 3 after adsorption for either 2 or 24 h at pH = 6

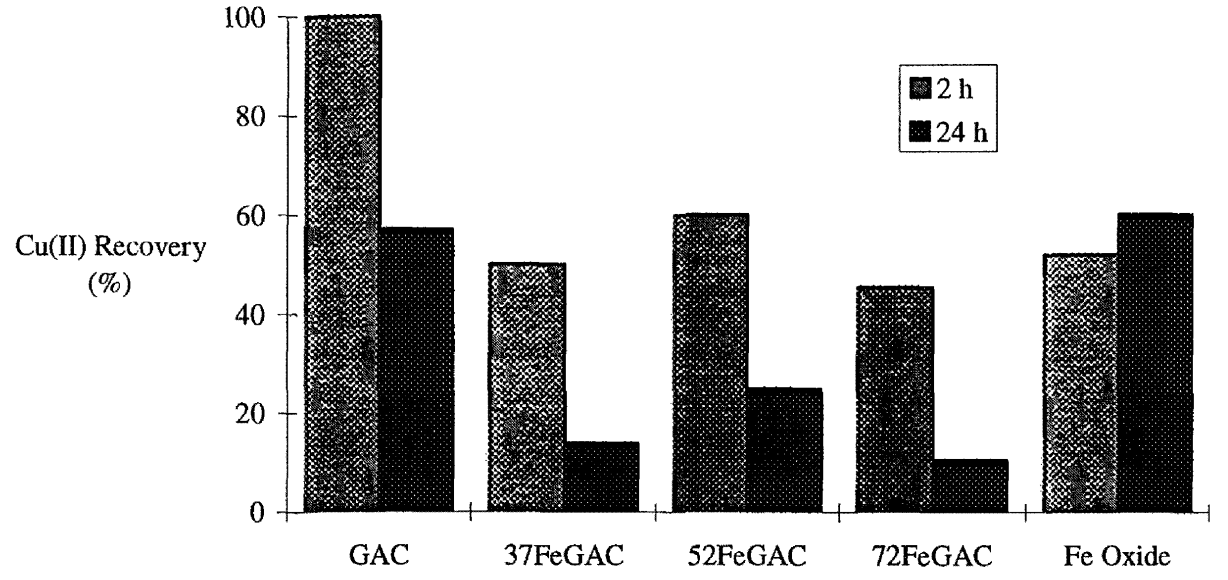
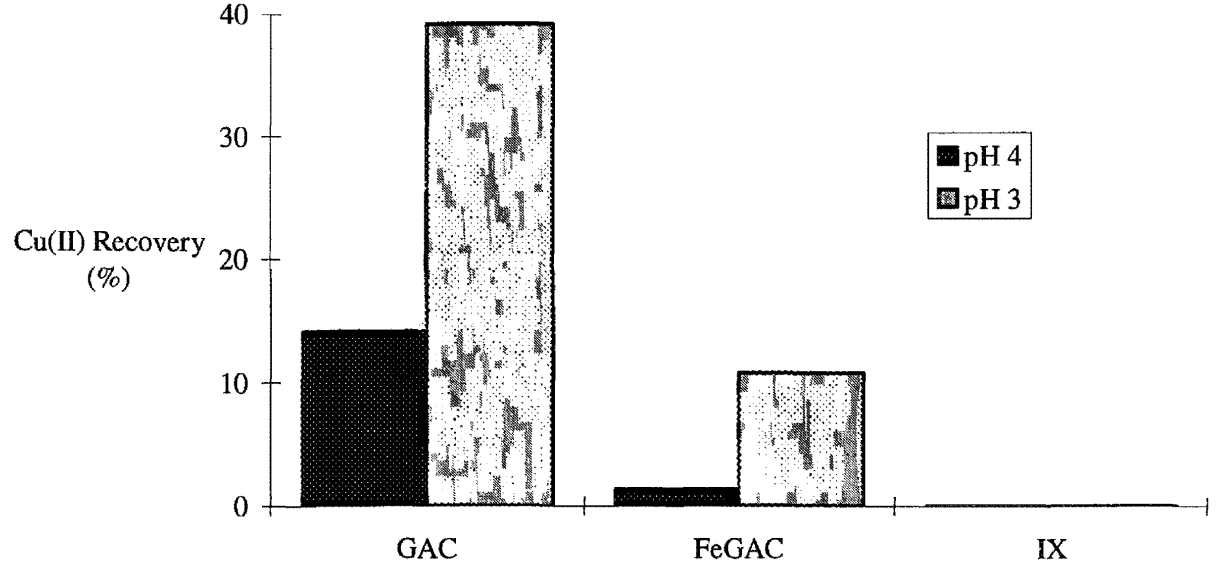


Figure 17 Cu(II) recovery from various media following a column adsorption test Desorption times were 24 h at pH = 4 followed by 1 h at pH = 3



Retention of adsorbed Cu(II) may influence the ability of the FeGAC adsorbent to be regenerated and reused To explore this possibility, a column was processed through a series of adsorption and

desorption cycles During these tests, the influent was a 0 01 M $NaNO_3$ solution containing Cu(II) (2 mg/L) and adjusted to pH 6 The flow rate was 5 mL/min and one cycle lasted for 200 bed volumes (10 h) At the end of the cycle, the influent was stopped and the column was regenerated for 2 h by recirculating through the column a 0 01 M $NaNO_3$ solution adjusted to pH 2 The regenerant solution was removed from the column and preserved for analysis, and a new adsorption cycle was started

A total of 15 cycles was processed (Figure 18) The highest effluent concentration was 0 5 mg/L and that occurred two times, at the end of cycles 2 and 9 The average effluent concentration throughout 3000 bed volumes was 0 06 mg/L, or 97% removal After 15 adsorption and desorption cycles, the adsorbent showed no signs of decreasing performance

In this same recycling experiment, the amount of Cu(II) recovered by the regeneration solution was compared to the amount of Cu(II) adsorbed in a cycle (Figure 19) Interestingly, regeneration efficiency increased with increasing cycle number, from only 30% in the first cycle to about 98% in cycle 15 In other words, the fraction of Cu(II) retained by the adsorbent decreased from about 60% in the first cycle to less than 5% in cycle 15 Furthermore, this retained Cu(II) apparently did not interfere with subsequent adsorption cycles As a result, the accumulated recovery efficiency, also shown in the figure, increased so that the fraction of retained Cu(II) became smaller with increasing number of cycles

Results from previous tests demonstrated that desorption of Cu(II) from FeGAC was a function of both the pH of the regeneration solution and the contact time during the adsorption step Figure 20 shows the results from another regeneration test after a column was loaded with low concentration influent (Cu(II) = 0 1 mg/L) In this case the regeneration pH was 1 7, and the test indicates that desorption elapsed time has little effect on the amount of Cu(II) recovered

Figure 18 Breakthrough curves for Cu(II) removal onto 37FeGAC through 15 cycles of regeneration Influent Cu(II) = 2 mg/L, loading = 5 mL/min, bed volume = 15 mL, influent pH = 6

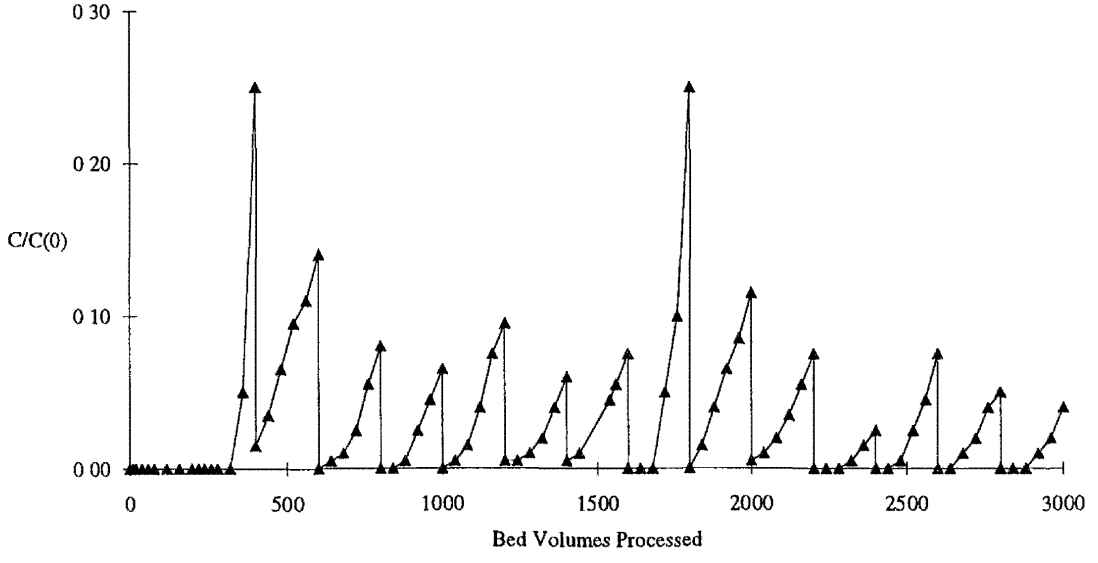


Figure 19 Recovery of adsorbed Cu(II) following removal onto 37FeGAC through 15 cycles Each cycle was regenerated at pH = 2 for 2 h

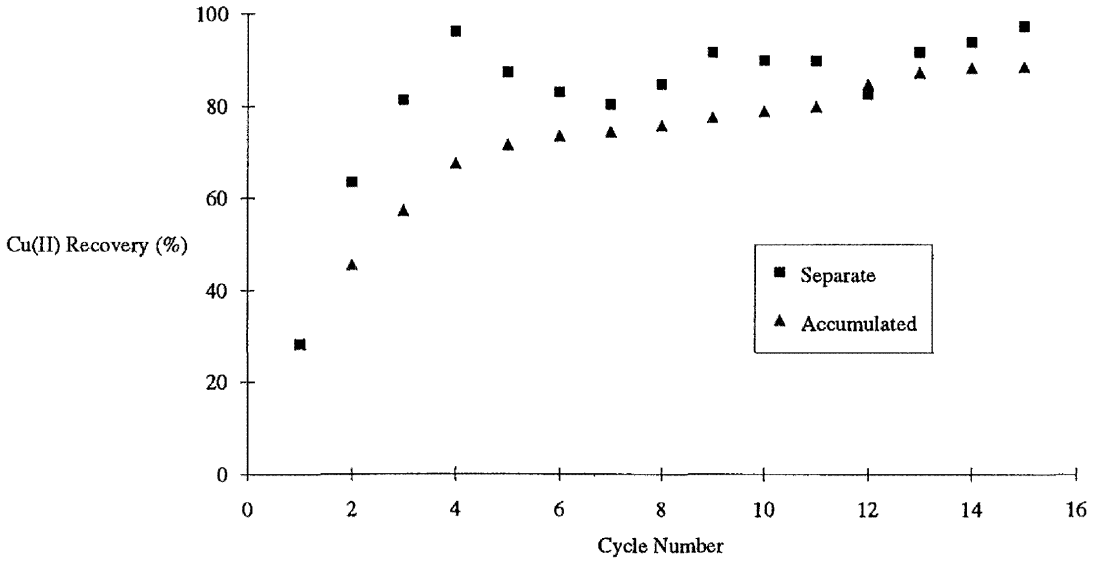
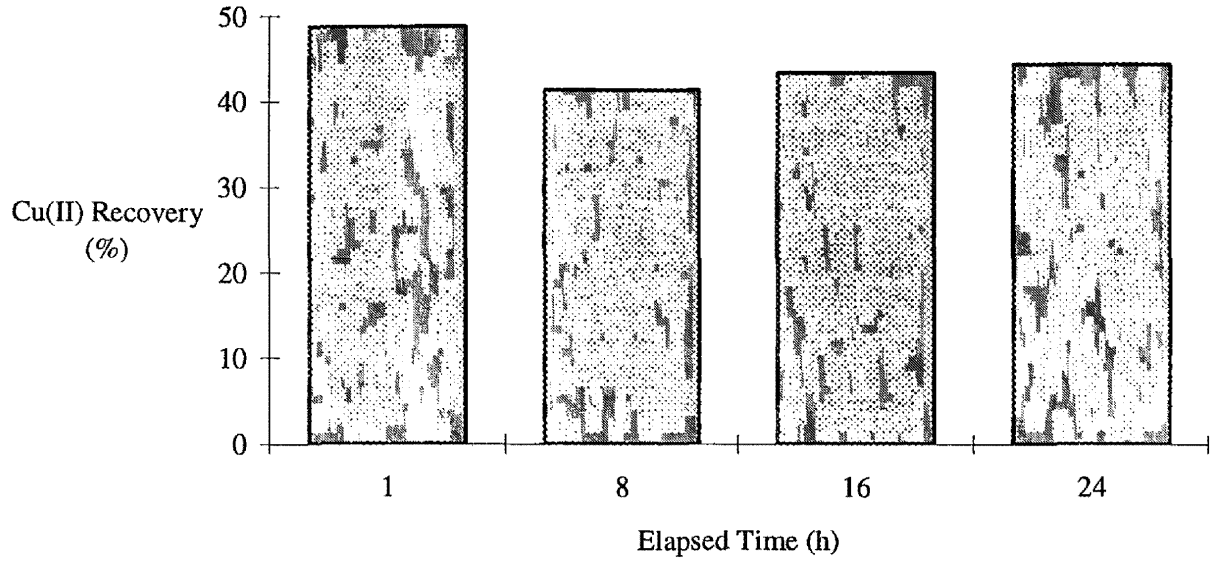


Figure 20 Recovery of Cu(II) after adsorption onto 37FeGAC Influent Cu(II) = 0 1 mg/L, loading = 5 mL/min, bed volume = 15 mL, influent pH = 6, and regeneration pH = 1 7



3 5 Adsoıbent Durability

The durability of the composite adsorbents was assessed in a series of tests in which the solids were maintained at one of three different pH values (Figure 21) After 24 h losses were less than 15% of the total Fe present With the exception of the 37 FeGAC sample at pH = 11, losses were greatei at low pH These concentrations, however, represent dissolved and colloidal (< 0 45 μm) Fe only, and it is possible that larger, discrete pieces of Fe oxide or Fe oxide-coated GAC were also present in the suspension

The adsorption/desorption cycling experiments also provided an opportunity to examine the durability of the composite adsorbent under simulated operating conditions In each of the first two cycles, the regeneration solution was analyzed for total Fe The results (Figure 22) indicate that the amount of Fe dissolved increased slightly duıing the 2 h desorption step at pH = 2 The total amount dissolved in one cycle was less than 0 1% of the Fe in the oxide coating The results also suggest that the Fe oxide becomes more difficult to dissolve as the number of cycles processed increases Only two cycles, however, were examined in these tests and additional experiments are required to validate this behavior

In contrast with the previous results suggesting that the amount of Cu(II) desorbed was not a function of elapsed desorption time, another test revealed that the amount of Fe lost from the coating did depend on exposure (Figure 23) Even though this regeneration condition was the harshest condition tested (lowest pH), the Fe loss was minimal There was a slight increase with increasing time for desorption, from 0 10% loss after 1 h up to almost 0 20% loss after 24 h

Figure 21 Fe lost in 24 h durability test at pH = 3, 7, or 11

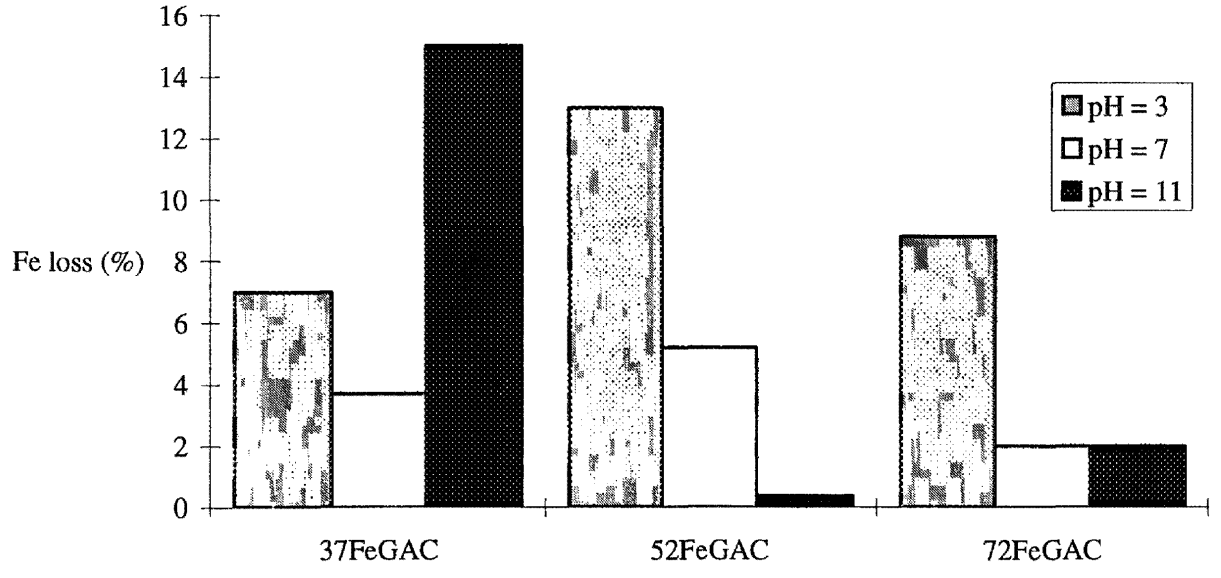


Figure 22 Loss of Fe from 37FeGAC as a function of time in two regeneration cycles Regeneration was at pH = 2

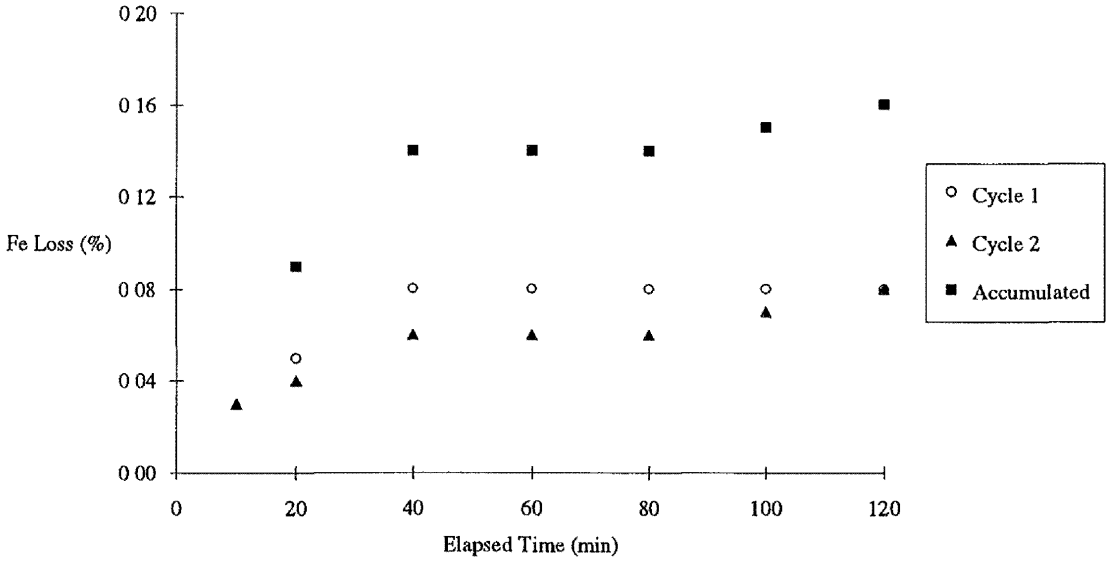
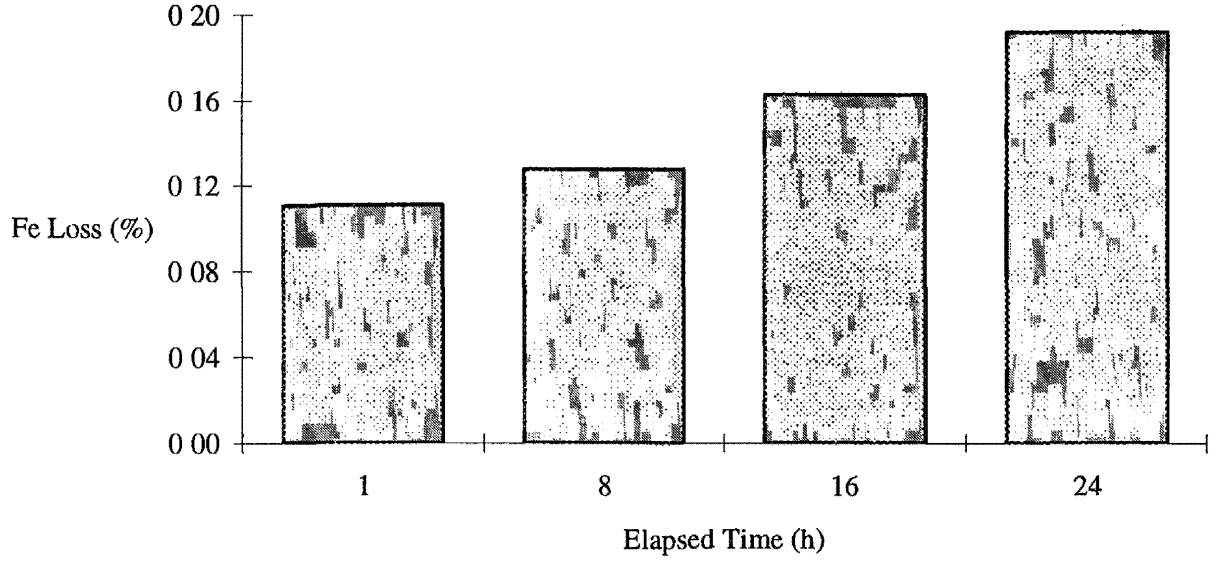


Figure 23 Fe loss as a function of time during regeneration of 37FeGAC Regeneration pH = 1 7



3 6 Adsorption from Low Concentration

One potentially attractive application of oxide-based adsorption processes is as a polishing step, in which metals can be removed to trace levels To evaluate the FeGAC adsorbent for processing low concentrations of metals, a feed solution containing 100 µg Cu(II)/L adjusted to pH = 6 was pumped through the column Based on the adsorption isotherm parameters calculated from the batch tests, the capacity of the column (7 g of 37 FeGAC in 15 cm^3 of bed) under these conditions should have been about 1 9 mg/g so that over 8,000 bed volumes could be processed before the column reached complete breakthrough Test results (Figure 24) are consistent with these predictions In the first 1,000 bed volumes processed the effluent Cu(II) concentration was no more than 3 µg/L in all samples

3 7 Effect of Complexing Ligands

The effect of complexation on the adsorption process was evaluated using three different ligands with a range of complexing ability Theoretical equilibrium speciation for the influent to the test column (0 01 M ionic strength, pH = 6) were calculated using MINTEQA2 (Allison et al , 1991), and the results are summarized in Table 4

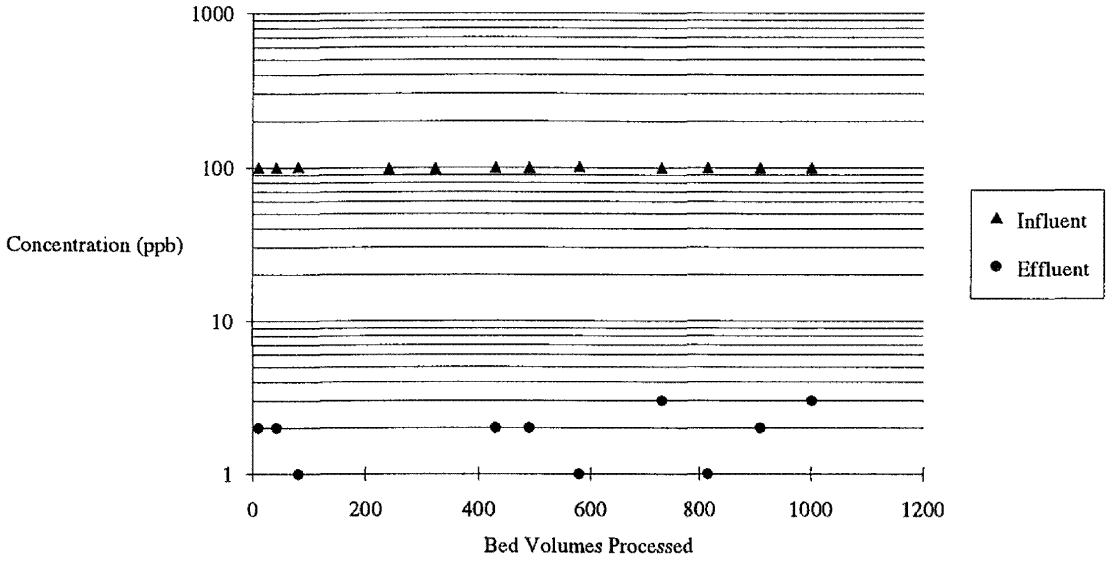
The fraction of Cu(II) complexed in these tests ranged from a minimal amount in the system with NO_3^- to a maximum of 100% in the system containing an equal molar amount of EDTA In these tests, the system with nitrate as the ligand serves as a control or reference system

In column tests with a complexing ligand, total Cu(II) removal can be viewed as removal of two separate species Removal of any free Cu(II) in the system should follow a pattern similar to the removal in the control experiment with nitrate Removal of complexed Cu(II) should depend on the characteristics of the complex Two extremes of behavior can be described One possibility is that relative to the ligand the oxide surface sites have a stronger affinity for Cu(II) In this case, the complex would be broken and the free Cu(II) would adsorb An alternative scenario is that the complex remains intact as a soluble species that has no affinity for the oxide surface In this case, total Cu(II) breakthrough in the column should resemble that of a conservative tracer Actual behavior could be somewhere between these extremes, depending on relative strength of the complex and surface site heterogeneties Furthermore, the possibility of some exposed GAC with the composite adsorbent used in these column tests may further modify system behavior

Table 4 Theoretical equilibrium speciation for the influent to the test columns Ionic strength = 0 01 M, $[Cu]_T$ = 3 17×10^{-5} M (2 mg/L), pH = 6

Ligand	mol/L	Fractional Cu Distribution		
		Cu^{2+}	Cu-ligand	$Cu(OH)^+$
NO_3^-	0.01	0.98	0	0.01
EDTA	3.17*10^{-5}	0	1.0	0
EDTA	1.58*10^{-5}	0.49	0.50	0.01
SO_4^{2-}	0.0035	0.76	0.23	0.01

Figure 24 Low level Cu(II) removal onto 37FeGAC Loading = 5 mL/min, bed volume = 15 mL/min, and influent pH = 6



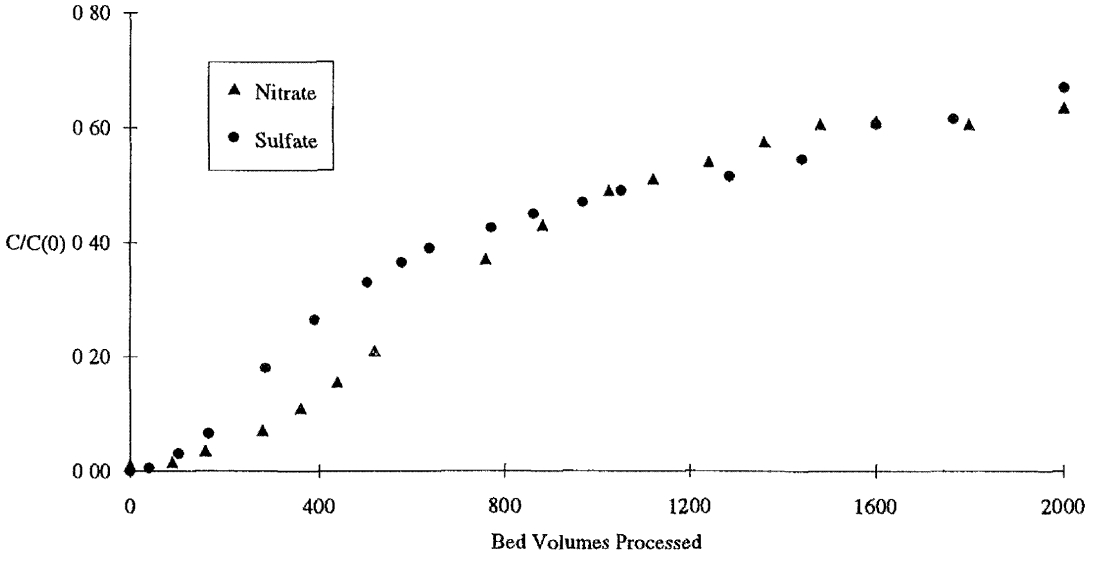
In one series of column adsorption tests, Cu(II) removal in the presence of sulfate was compared to Cu(II) removal in the presence of nitrate (Figure 25) For both systems there was nearly complete removal of total Cu(II) through the first 100 bed volumes processed Because nearly one-quarter of the Cu(II) in the sulfate system was complexed (Table 4), this result indicates that either the complex was broken (and free Cu(II) adsorbed) or the complex was adsorbed within the column In either case, total Cu(II) was not retained as well as in the nitrate system because as additional bed volumes were processed, breakthrough occurred first in the system with sulfate Based on the areas above the breakthrough curves, the adsorption capacities in these two systems through 1800 bed volumes was 3 86 mg/g and 4 11 mg/g for the sulfate and nitrate systems, respectively

Interestingly, the breakthrough curves for these two systems appear to converge after about 900 bed volumes The shape of the breakthrough curve for the sulfate system is actually a composite curve representing the breakthrough of first Cu(II) from the complex and then free Cu(II) As C/C_o increases from 0 to about 0 25, breakthrough is primarily due to the $CuSO_4$ complex Beyond that point, a breakthrough curve for free Cu(II) should be superposed to complete the composite figure The superposed breakthrough curve, however, is different from that of the reference $Cu(NO_3)_2$ system because the $CuSO_4$ system contains less free Cu(II) As a result of this lower concentration, more bed volumes need to be processed to achieve the same capacity on the adsorbent In effect, the breakthrough curve for free Cu(II) removal is "stretched out" relative to the reference system

In another series of tests, total Cu(II) removal in the presence of EDTA was compared with the reference $Cu(NO_3)_2$ system When an equal molar concentration of EDTA was added and presumably all the Cu(II) was complexed, breakthrough was relatively rapid (Figure 26), approaching 100% after 500 bed volumes were processed In a system with the EDTA Cu(II) molar ratio = 0 5, the same type of composite breakthrough curve observed for the $CuSO_4$ system is evident Over the first 200 bed volumes, the breakthrough curve is primarily due to the Cu(II)-EDTA complex Relative to the previous

test, however, this breakthrough curve is stretched out because the concentration of the complex is only half of the previous value After about 200 bed volumes, the breakthrough curve actually begins to represent both species of Cu(II), the Cu(II)-EDTA and free Cu(II)

Figure 25 Influence of SO_4^{2-} (0 0035 M) on the removal of total Cu(II) by 37FeGAC Influent total Cu(II) = 2 mg/L, loading = 5 mL/min, bed volume = 15 mL, and influent pH = 6



Previous studies of metal adsorption onto soils (Bowman, et al , 1981, Elliott and Denneny, 1982) concluded that relative to systems containing free metal, adsorption of metals complexed by EDTA was significantly reduced If so, Cu(II) removal in our column experiments must be primarily due to exposed GAC To test this, a similar experiment was conducted with untreated GAC Relative to the GAC system, breakthrough for the 37FeGAC system was slightly faster (Figure 27) After 500 bed volumes, the calculated capacities for these two systems were 0 46 mg/g (37FeGAC) and 0 48 mg/g (GAC) This result suggests that at least from the perspective of the Cu(II)-EDTA complex, the amount of the GAC surface available for adsorption was approximately the same whether the untreated GAC or 37FeGAC was present

Figure 26 Influence of EDTA on removal of total Cu(II) by 37FeGAC Influent total Cu(II) = 2 mg/L, loading = 5 mL/min, bed volume = 15 mL, influent pH = 6

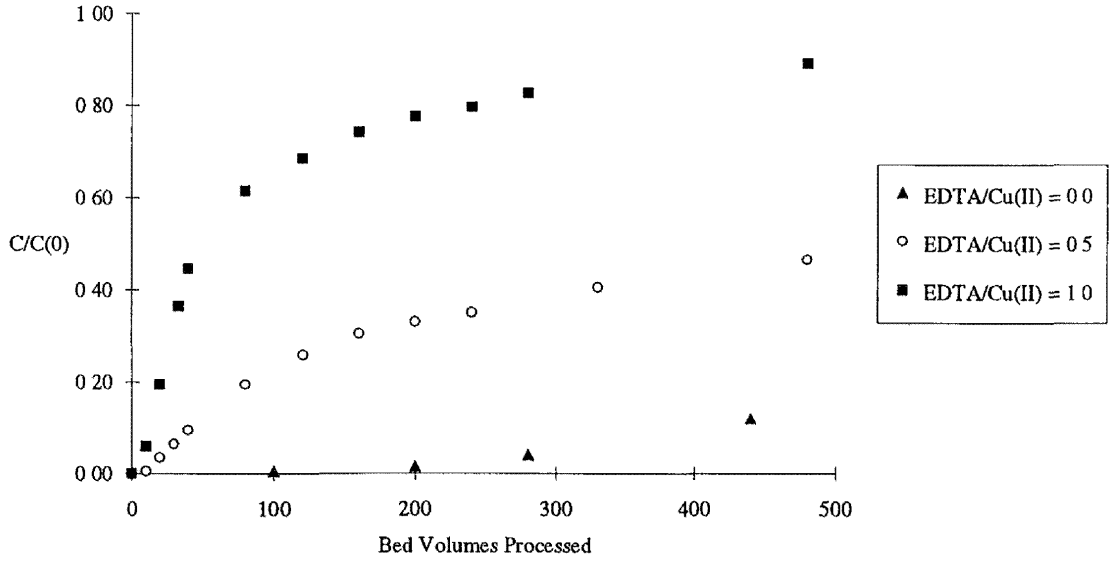
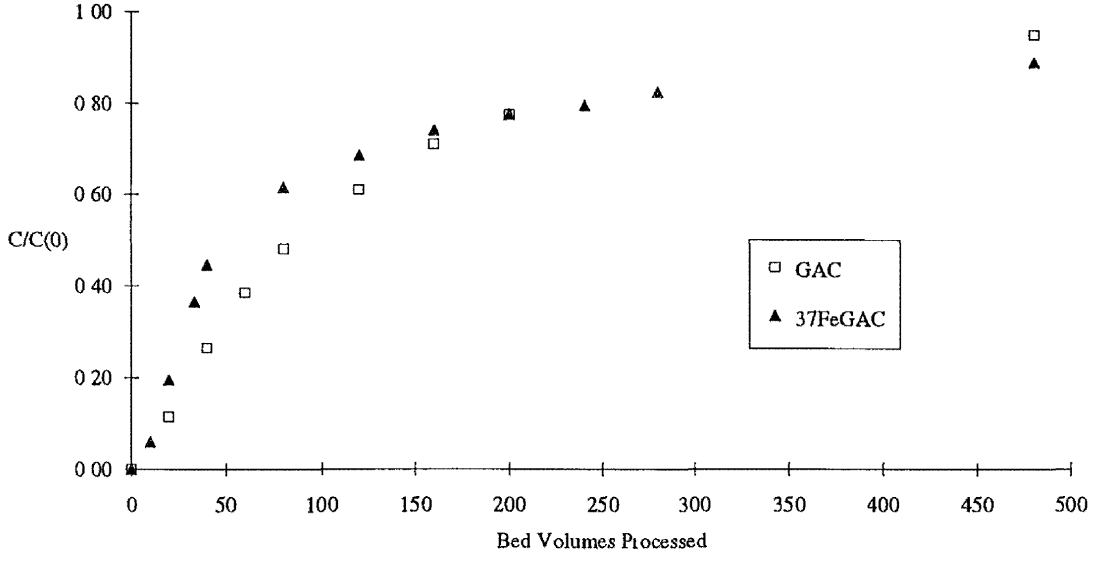


Figure 27 Adsorption of the EDTA-Cu(II) complex by GAC and 37FeGAC Influent total Cu(II) = 2 mg/L, loading = 5 mL/min, bed volume = 15 mL, influent pH = 6



4 0 Discussion

The ability of the composite adsorbent to remove and recycle adsorbates from solution depends on the adsorbate In these studies, although Cr(VI) could be removed from solution by either Fe oxide or GAC, adsorption capacity decreased with increasing Fe oxide deposits on the GAC surface In contrast, Cu(II) adsorption capacity increased with increasing Fe oxide surface coating Reasons for these differences are not clear Reduction of Cr(VI) to Cr(III) at the GAC surface is possible, but according to Bowers and Huang (1987), this reduction reaction is unlikely in the pH range studied in these experiments

The adsorption capacity for Cu(II) increased from 1 3 mg/g for GAC to about 5 mg/g for 37FeGAC Although column tests with 72FeGAC were not conducted, the results of the batch adsorption tests suggest this composite adsorbent would have a capacity of about 7 mg Cu(II)/g Although these capacities are considerably less than the approximately 100 mg/g estimated for the ion exchange resin, these tests did not identify an upper limit for the Fe oxide coating Furthermore, alternative coating processes might result in an Fe oxide surface with increased capacity

Although some Cu(II) was retained by the composite adsorbent during regeneration, the residual adsorbate did not interfere with subsequent adsorption cycles In fact, tests through several cycles demonstrated that the fraction of slowly reversible adsorbate actually decreased with increasing cycles It seems that a fraction of the surface binding sites are high energy, slowly reversible or irreversible sites that accumulate Cu(II) during each adsorption cycle Even when these sites become full, other lower energy, reversible sites are still able to adsorb and desorb Cu(II) through numerous cycles None of the adsorption cycling tests, however, ran until the column reached 100% breakthrough, and the site characteristics may change when the adsorbent is fully loaded This concept seems to be supported by results suggesting that surface precipitation may play a role in adsorbate removal

Effective regeneration using a small volume adjusted to pH = 2 may be a significant advantage relative to ion exchange processes A typical ion exchange process would be regenerated with a solution of either 10% H_2SO_4 or 15% HNO_3 (Reynolds, 1982)

The composite adsorbent performed well during tests conducted at low influent Cu(II) concentrations Removal was consistently down to trace levels, and it seems likely that regeneration could be used to concentrate Cu(II) to levels appropriate for recovery by other techniques

Finally, removal of complexed Cu(II) depends on the ligand and the characteristics of the complex Even when a very strong ligand such as EDTA was present removal was possible but the capacity for total Cu(II) removal decreased from about 5 mg/g to about 0 5 mg/g Adsorption of the Cu(II)-EDTA complex was probably due to exposed GAC

5 0 Conclusions

Fe oxide-coated GAC performed well as a composite adsorbent for the removal of low levels of Cu(II) from solution Results from these studies indicate that this solid can be used in column adsorption processes to not only remove but also recover adsorbed Cu(II) This technique looks especially promising for treatment to low levels, a column loaded with 100 μg Cu(II)/L produced an effluent with no more than 3 μg Cu(II)/L through 1000 bed volumes processed Removal capacities of at least 5 mg Cu(II) per g adsorbent were achieved in column tests The adsorbent was regenerated using a solution adjusted to pH = 2 and the amount of Cu(II) recovered increased from about 30% in the first cycle to over 90% in subsequent cycles Retention of adsorbed Cu(II) by solid did not interfere with subsequent adsorption steps through 15 cycles

The composite adsorbent was ineffective at removing Cr(VI) anionic species from solution In fact, tests indicated that Fe oxide-coated GAC was a less effective adsorbent than either Fe oxide or GAC by themselves This unexpected behavior and other questions generated in this research are addressed in the next section

6 0 Recommendations

Results from these tests suggest several areas for additional research A number of questions are concerned with how adsorption is influenced by substrate properties such as surface area and pore volume distribution Ash components on the GAC probably affect the surface chemistry also, so the need to pretreat the substrate should be assessed In this study, only one Fe oxide synthesis pathway was explored Other options such as oxidation or precipitation in the presence of other ions will generate oxides with different properties that may have greater affinities for some metals

The behavior of Cr(VI) remains to be explained As the mechanisms for inhibited removal become clear, they should open the pathways to enhanced or selective adsorption Other cationic and anionic metal species should be evaluated to determine how selective the process is and if surface precipitation does occur Solutions containing multiple adsorbents need to be tested to better understand the role of cocontaminants on adsorption

Regeneration and recycling are potential advantages associated with an Fe oxide-coated GAC adsorbent Iron loss through extended cycles should be measured It may also be possible to reuse the regeneration solution through many cycles, minimizing disposal costs and significantly concentrating the desorbed metals

Finally, the economic aspects of treatment with Fe oxide-coated GAC need to be quantified As the regeneration and recycle potential become clearer, it should be possible to compare capital and operating costs to other treatment technologies, such as ion exchange, to demonstrate the usefulness of the process

7 0 References

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8 0 Appendices

A Project Quality Assurance Plan

A quality control form was developed for this project to monitor and record calibration, analysis of reagent blanks, analysis for recovery of known additions, and analysis of duplicates The quality control plan specified 10% of the samples would be analyzed for recovery of known additions, an independently prepared standard would be prepared and submitted for analysis each day that samples were analyzed, 5% of the samples analyzed would be a reagent blank, 5% of the samples would be analyzed in duplicate, and at least three dilutions of the standard would be analyzed immediately before and immediately after sample analysis A representative copy of a Quality Control Sheet is attached

In addition, these quality control procedures were complemented by submitting samples to the HWRIC Hazardous Materials Laboratory for laboratory intercomparison The results of those analyses are summarized in the following tables (Precision was calculated relative to the mean of the two values)

From October, 1992

Sample	IIT (mg/L)	HWRIC (mg/L)	Precision (%)
Fe - 1	40	35 1	86 9
Fe - 2	50	44 0	87 2
Fe - 3	80	73 6	91 7
Cu - 1	0 08	0 08	100
Cu - 2	1 05	1 05	100
Cu - 3	1.45	1.29	88.3

From May, 1993

Sample	IIT (mg/L)	HWRIC (mg/L)	Precision (%)
Fe - 1	2 2	2 0	90 5
Fe - 2	2 2	2 0	90 5
Fe - 3	2 2	2 0	90 5
Cu - 1	2 0	1 95	97 5
Cu - 2	1 4	1 3	92 6
Cu - 3	9 2	8 95	97 2
Cr - 1	10 5	11 1	105 5
Cr - 2	10 0	8 95	88 9
Cr - 3	8 0	7 37	91 8

The acceptance level for high-level duplicates is 90 - 110% (Clesceri et al , 1989) In the initial analyses of October, 1992, two of the Fe samples and one of the Cu samples failed to meet the acceptance level In the more recent analyses of May, 1993, one of the Cr samples failed to meet the acceptance level